

Vowels	INSROT	Proposed
अ	a	a
आ	aa or A	aa
इ	i	i
ई	ii or I	ii
उ	u	u
ऊ	uu or U	uu
ऋ	RRi or R [~] i	r'i
ॠ	RRI or R [~] I	r''i
ऌ	LLi or L [~] i	l'i
ॡ	LLI or L [~] I	l''i
ए	e	e
ऐ	ai	ai
ओ	o	o
औ	au	au
अं	aM	am
अः	aH	ah

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Scanning tunneling microscopy and spectroscopy of C₇₀ thin films

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Abstract. Scanning tunneling microscopy of C₇₀ thin films on various substrates has been carried out to investigate the 2D packing of the molecules, providing direct evidence for orientational disorder, high resolution images of the carbon skeleton as well as the molecular arrangement in the films. Tunneling spectroscopy is also presented. Tunneling conductance measurements indicate the presence of C₇₀ molecules deposited on HOPG substrate.

Keywords. C₇₀; fullerenes; orientational disorder; scanning tunneling microscopy; spectroscopy.

1. Introduction

Scanning tunneling microscopy (STM) has emerged as a powerful technique for the study of solids and surfaces at atomic resolution. STM studies have been carried out on the morphology, local structure as well as the nature of the electronic states. This technique has been used recently for the study of fullerene molecules. C₆₀, has been studied by STM in considerable detail (Weaver 1992), high resolution images showing details of the cage molecule. Orientational disorder in C₆₀ also seen in STM studies, although the spherical nature of the molecule makes it

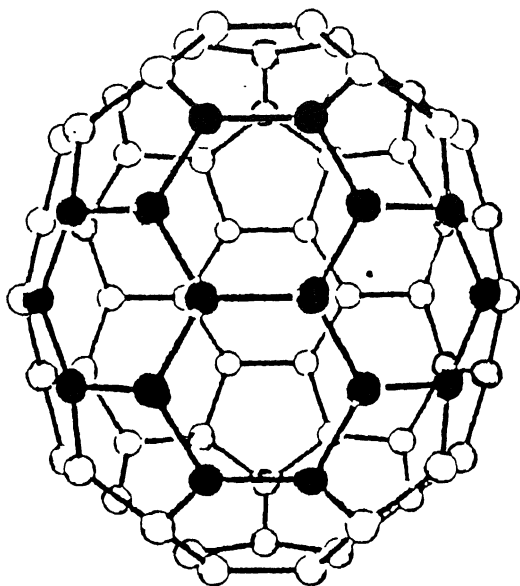


Figure 1. Structure of C_{70} .

2. Experimental

C_{70} was prepared by the contact arc evaporation of graphite at 1 atm. This evaporation technique first yields a mixture of C_{60} and C_{70} . This mixture was then extracted with CS_2 , C_{70} was separated from the mixture by column chromatography (Govindaraj and Rao 1993). C_{70} thus obtained was pure. Further purification was carried out by column chromatography on alumina with 5% toluene in petroleum ether solvent. The purity of C_{70} in this way was above 99% which was confirmed by UV-Vis spectroscopy. The melting point of C_{70} is 473 K.

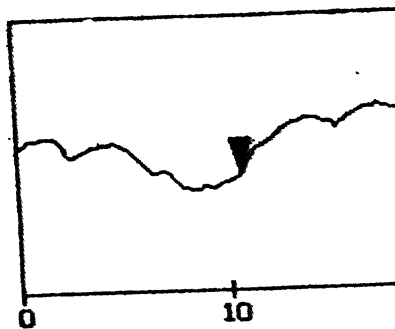
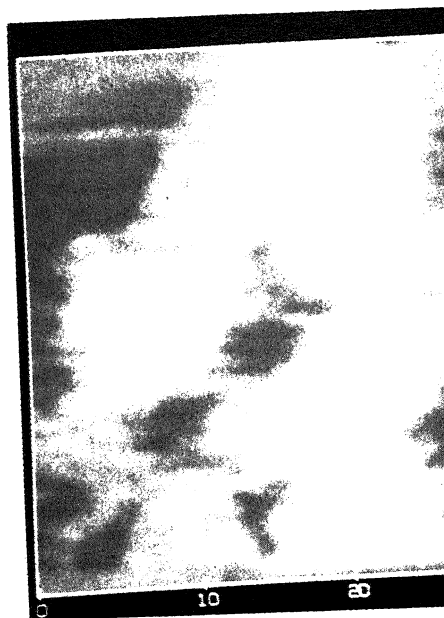
STM and spectroscopy of C_{70} thin films

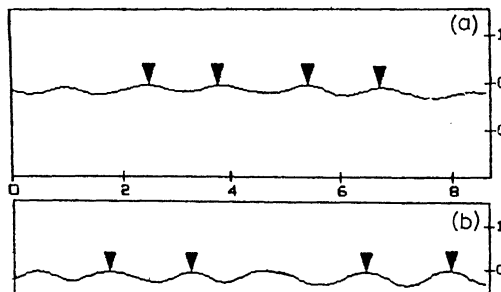
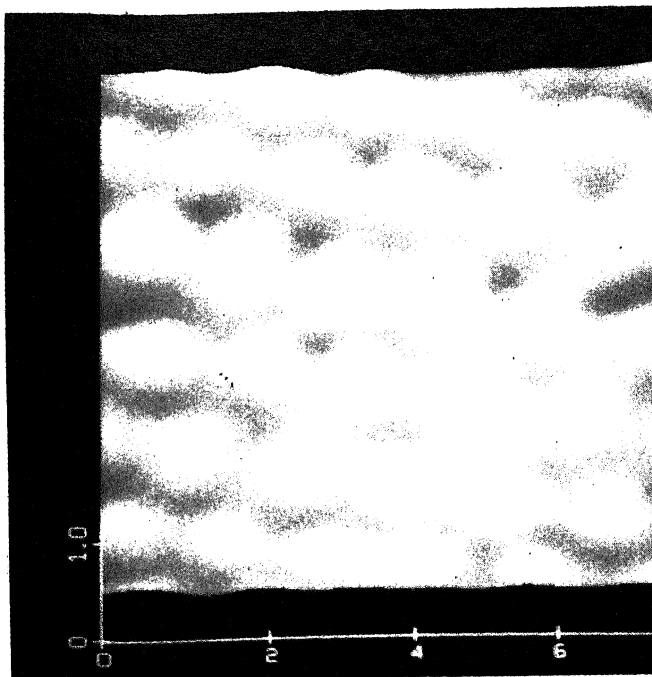
well as gold substrate possibly as a result of charge transfer to the film which renders it sufficiently conducting for STM.

We show a typical low magnification STM image of C_{70} on HOPG in figure 2a. The image shows uniform C_{70} coverage with microcrystallites typically of 10–15 nm. Each such microcrystallite contains 10–12 molecules with the spacing between individual molecules which agrees well with the hexagonal packing arrangement of the film varies between 2–4 nm. In figure 2b, we show the surface step with a step height of 0.8 nm which also shows some brighter spots in such islands which are at the early stage of growth of a second layer before the completion of the first layer. The variation in the heights of features within an island reveals a small amount of disorder in the film.

We show a lattice-resolved STM image of a C_{70} film on HOPG in figure 3. The image clearly shows the ellipsoidal molecules. Line profiles taken across the minor and major axes show the size of a typical molecule to be 1.07 nm $\times$ 1.17 nm with the aspect ratio less than 1 as expected. We will be discussing the lattice-resolved STM images of these films later in the discussion.

Scanning tunneling spectroscopic (STS) measurements were taken at various points on the C_{70} film deposited on HOPG by open circuit technique, monitoring the current [and normalized conductance (dI/dV)] as a function of the bias voltage over a range. With the active feedback, the bias voltage is ramped over a range, at fixed tunneling current, the tip height adjusts itself. With the increase in voltage, the lateral resolution improves with the decreasing voltage the conductance (dI/dV) increases in the zero bias region. This problem was overcome by open circuit technique by measuring the I - V curves at a constant tip-sample distance. The tip-sample transmission factor (which distorts the features) is eliminated by plotting the normalized conductance,



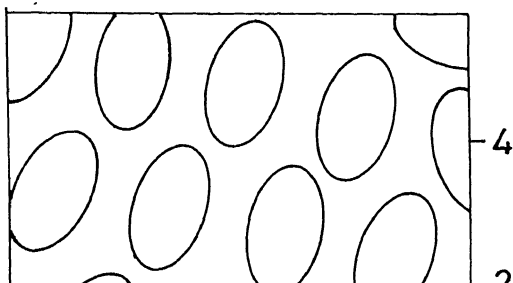
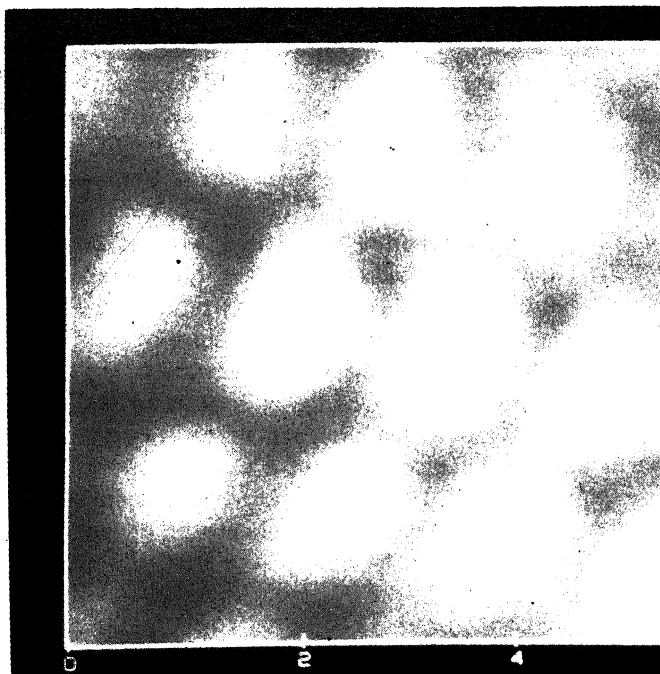


STM and spectroscopy of C_{70} thin films

These spacings are only slightly different from the expected value of 1.68 nm along the two directions. This can arise from orientation of individual molecules or due to C_{70} -HOPG interaction (Liu *et al.* 1994). Profiles along the minor and major axis of a typical ellipsoid are shown in figures 4c and d however indicate the aspect ratio to be 1.1, exactly confirming the D_{5h} structure of the C_{70} molecule when oriented along to its five-fold symmetry axis.

Orientational disorder of C_{70} has been reported by several authors (for example Ramasesha *et al.* 1994, Rao and Seshadri 1994). The C_{70} phase of C_{70} is orientationally disordered as confirmed by Raman measurements which show the molecules to be rotating anisotropically with temperature (Fischer and Heiney 1993). Because the C_{70} molecule is of rugby-ball shape, we can readily see disorder in terms of the orientation of the long axis. STM images of C_{70} films/HOPG show the presence of orientational disorder. In figure 5, we show a zoomed lattice image of a C_{70} film showing ellipsoidal molecules with an aspect ratio of 1.1. This image clearly shows the presence of orientational disorder, i.e. differences in the orientation of the molecules with respect to one another. This can be clearly seen in the image corresponding to the image given in figure 5. We also show a different configuration (i.e. the long axis perpendicular to interface) of C_{70} molecules. This configuration of C_{70} is expected for an hcp arrangement. In figure 6, a lattice-resolved image from a different area of the C_{70} film shows that the molecules are orientationally different from one another as can be seen in the marked portion in the lower half of the image.

The STM image of the C_{70} film in figure 7 shows the presence of a grain boundary between two different regions of the C_{70} lattice. The arrow in the image indicates the location of the grain boundary. High-resolution STM images of C_{70} films generally showed a disordered hcp lattice arrangement with no other apparent defects. However, on scanning different areas of the film at the atomic scale, the sample showed some regions containing defects. In figure 8, we show an area with a defect which is also



STM and spectroscopy of C_{70} thin films

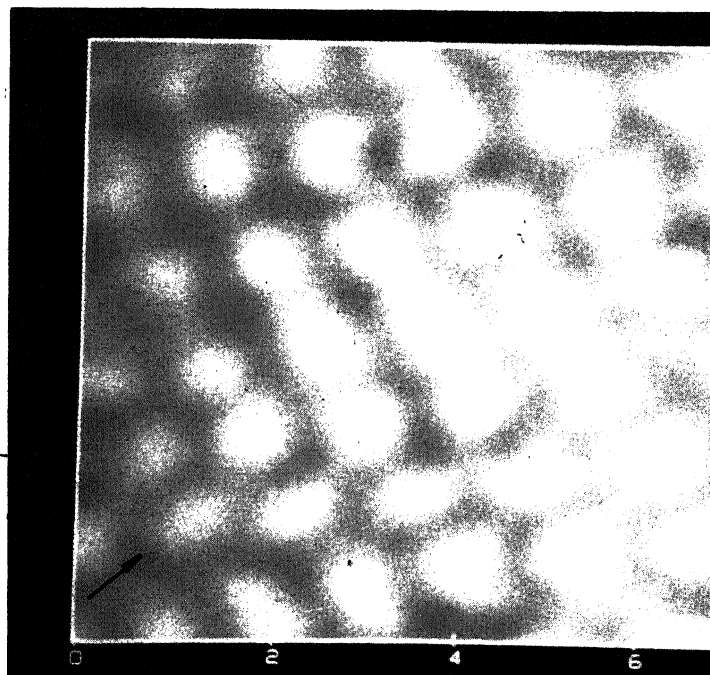
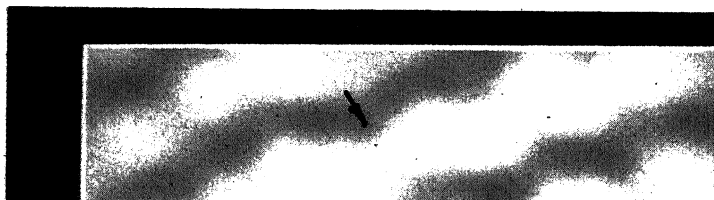
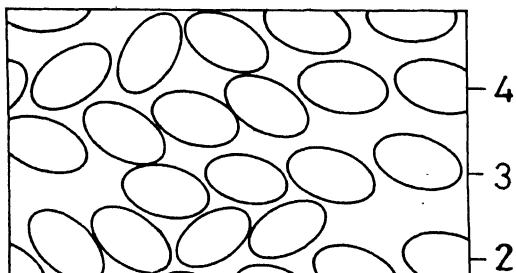
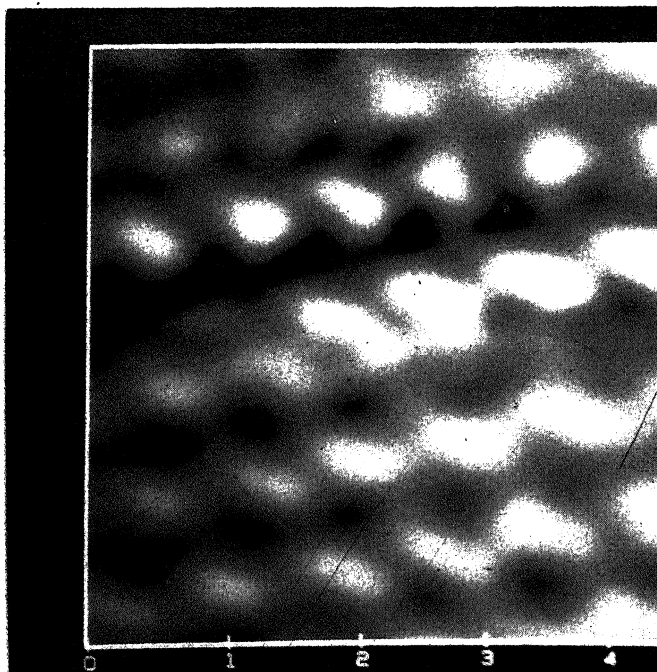
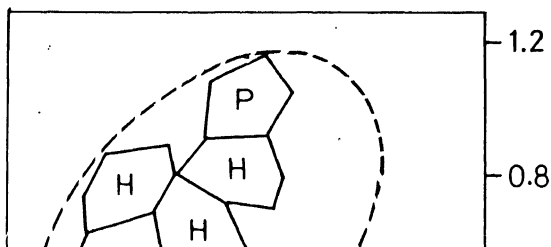
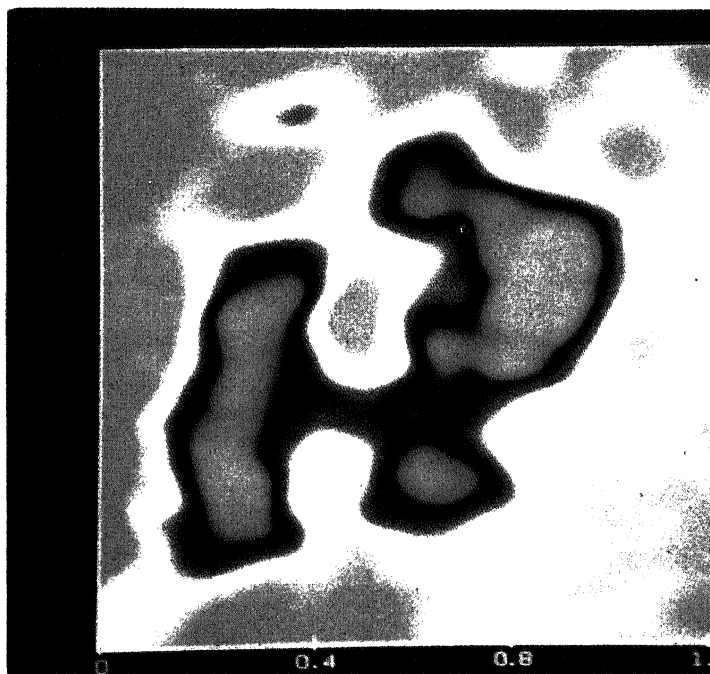


Figure 6. STM image ($6.89\text{ nm} \times 6.89\text{ nm}$) of C_{70} lattice of HOPG. The arrow shows orientational disorder.





STM and spectroscopy of C₇₀ thin films



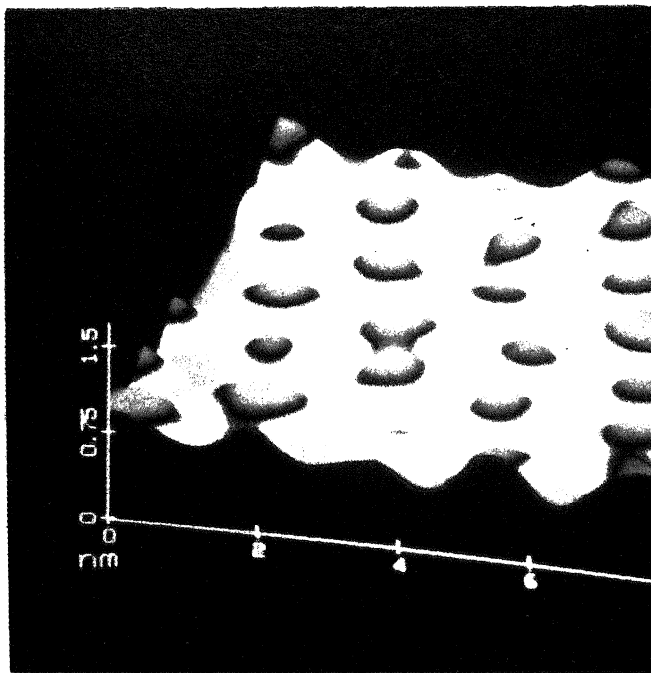
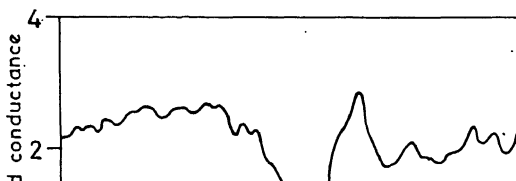


Figure 10. Typical STM surface plot (in 30° pitch) of HOPG.



STM and spectroscopy of C₇₀ thin films

the observation that STM images were acquired at a bias HOMO-LUMO gap of 1.6 eV for C₇₀.

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YBa₂SnO_{5.5}, a novel ceramic substrate for BiSCCO superconductors

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Abstract. YBa₂SnO_{5.5} has been synthesized and sintered and used as substrate for both YBCO and BiSCCO superconductors. The cubic perovskite (A₂BB'O₆) structure with the lattice constant a_p and loss factor of YBa₂SnO_{5.5} are in a range suitable for microwave applications. YBa₂SnO_{5.5} is found to be chemically stable with YBCO and BiSCCO superconductors. The thick film of YBCO screen coated on YBa₂SnO_{5.5} substrate gave a $T_{c(0)}$ of 92 K and a critical current density of 3 × 10³ A/cm² at 77 K. A screen printed BiSCCO thick film on YBa₂SnO_{5.5} substrate gave a $T_{c(0)}$ of 85 K and a critical current density of 3 × 10³ A/cm² at 77 K.

Keywords. Ceramic substrate; YBa₂SnO_{5.5}.

1. Introduction

Since the discovery of high T_c superconductors, there has been a great interest in producing these materials in thick and thin film forms. Substrates play a vital role in the preparation of superconducting films. The non-reactivity between the substrate and superconductor at the interface is the most crucial factor for obtaining a high T_c superconductor (Rowell *et al* 1988; Rowell 1991). In addition, for the microwave applications, the substrates should have low dielectric constant and loss tangent. The available substrates such as Si, SiO₂, Ge, Al₂O₃ etc react with

$J_c = 3 \times 10^3$ A/cm² at 77 K. In the present paper, we describe YBSO as a polycrystalline substrate material for microwave non-reactivity with BiSCCO superconductors and the fabrication of BiSCCO superconducting thick films on this substrate.

2. Experimental

YBa₂SnO_{5.5} was synthesized following the conventional solid state reaction. High purity (99.9%) Y₂O₃, BaCO₃ and SnO₂ were wet milled using an agate mortar. The mixed powder was pressed into pellets. It was calcined in air at 1150°C for 72 h with three intermediate calcination with multiple grindings was essential to get a uniform calcined material was then finely ground and pelletized again in the form of circular discs having 11 mm dia and 2 mm thick. The pellets were sintered at 1400°C for 12 h in air. The structure was examined by X-ray diffraction (XRD) method using a Siemens D5000 Diffractometer with nickel filtered CuK α radiation. The dielectric factor of YBSO were measured using an HP 4192 A Computerized Impedance Analyzer in the frequency range 30 Hz to 13 MHz at room temperature on both sides of the pellet.

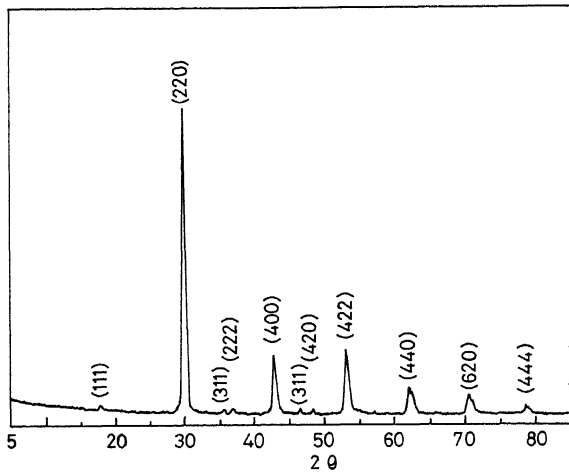
Thick film paste of YBCO for screen printing was made by mixing YBCO powder (prepared by standard solid state reaction) with a binder. The viscosity of the thick film paste was controlled by the addition of available fish oil. This paste was screen printed on the substrate using a screen of 325 mesh size. The printed film was fired in a furnace in air at a rate of 2°C/min to 980°C. The film was cooled at 0.2°C/min to 940°C and was kept at this temperature for 1 h to room temperature at a rate 1°C/min. Heating up to 980°C for good adhesion and slow cooling at 1°C/min from 940°C to room temperature is essential for oxygenation.

For screen printing BiSCCO films, a thick film paste of Bi-2223 (pure Bi(2223)) powder prepared from the nominal composition

YBa₂SnO_{5.5} as substrate for YBCO and BiSCCO

for a complex cubic perovskite (A₂BB'O₆) structure with 8.430 Å and the computerized XRD data of YBa₂SnO_{5.5} is DTA experiment carried out using a Shimadzu DTA-50 H there is no phase transition in YBSO material up to a temp sintered density of YBSO as measured by Archimedes m theoretical density (6.12 g/cm³) and the room temperature r 10¹⁰ Ω cm. The electrical resistivity and density of the h samples were same as that of the sintered sample indicating stable under atmospheric conditions. The YBSO samples w and could be sliced into thin pieces of 0.5 mm thickness by reflecting surfaces were obtained by mechanical polishing an as alcohol, acetone, carbon tetrachloride could be used as et

The dielectric constant (ε') and loss factor (tan δ) of YB frequency range 10 Hz to 13 MHz at room temperature and



$\tan \delta$ are shown in figure 2. The dielectric constant of YBSO are comparable to those of MgO at these frequencies. If we consider YBSO as a simple perovskite unit cell, the lattice constant of YBSO is smaller than that of MgO. The melting experiments conducted on YBSO indicate that this material melts congruently and could be grown from the melt.

One of the most important criteria for the selection of YBSO as a substrate for YBCO and BiSCCO superconductors is the chemical compatibility and the superconductor films at the processing temperature. The chemical non-reactivity of YBSO with YBCO has already been reported in the literature (Koshy *et al* 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024, 2025). The chemical compatibility between YBSO and BiSCCO has been confirmed by mixing 20 vol% of YBSO in Bi(2223) and annealing at 850°C for 20 h and figure 3 (curve C) shows the XRD pattern of the YBSO-Bi(2223) sample. The XRD pattern of the two phases in the annealed sample is compared with those of pure Bi(2223) (figure 3, curve A) and pure YBCO (figure 3, curve B) samples. Figure 3 shows that there is no additional phase formed other than those of Bi(2223) and YBCO in the annealed YBSO-Bi(2223) composite (within the precision of the XRD technique). This indicates that YBSO is chemically compatible with Bi(2223).

The suitability of YBSO as substrate for YBCO and BiSCCO superconductors was confirmed by screen printing YBCO and BiSCCO on YBSO polycrystalline substrate. Figures 4a and b show the XRD patterns of BiSCCO thick films developed on YBSO substrates. Figure 4a shows the peaks of YBSO, all the other peaks in figure 4a are due to the superconducting YBCO. However in the case of BiSCCO, the printed film contained both Bi(2223) (~ 80 vol%) and Bi(2201) (~ 20 vol%).



YBa₂SnO_{5.5} as substrate for YBCO and BiSCCO

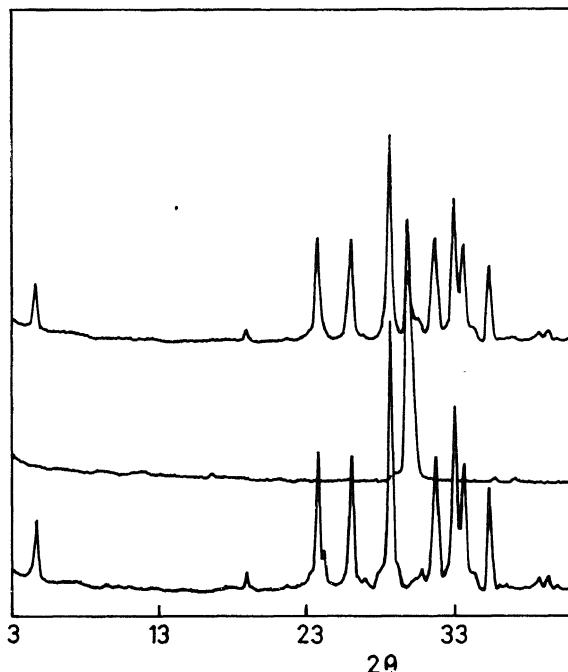
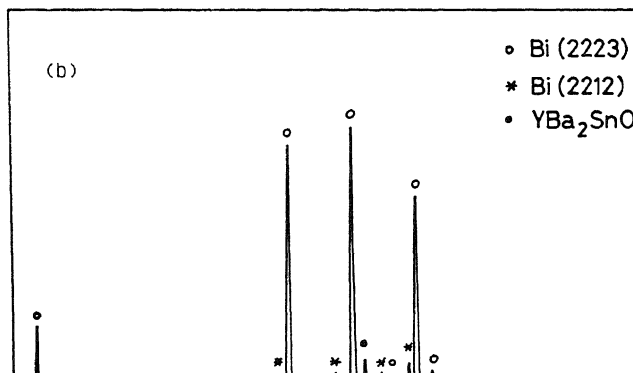
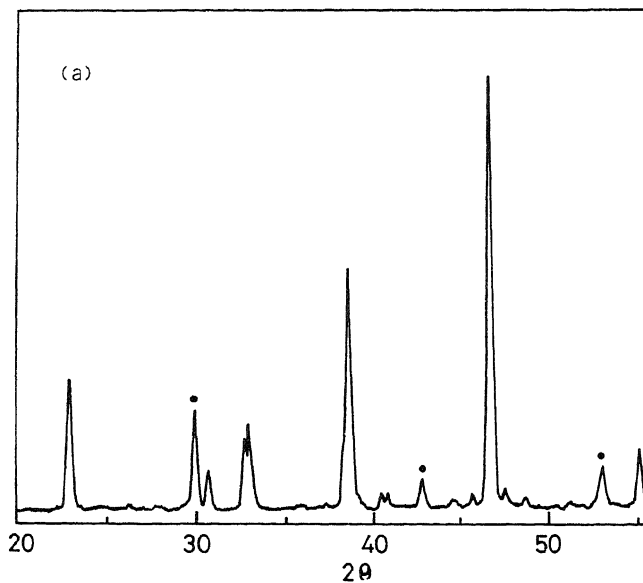


Figure 3. X-ray diffraction pattern for (A) Bi(2223) superconductor, (B) Bi(2223) superconductor on YBa₂SnO_{5.5} substrate, and (C) 4 : 1 volume mixture of Bi(2223) and YBa₂SnO_{5.5}.

The formation of Bi(2212) phase may be due to the partial reduction of Bi(2223) phase during the thick film processing at 880°C. The volume fraction of Bi(2212) phase in the BiSCCO thick film were determined by X-ray diffraction.



YBa₂SnO_{5.5} as substrate for YBCO and BiSCCO

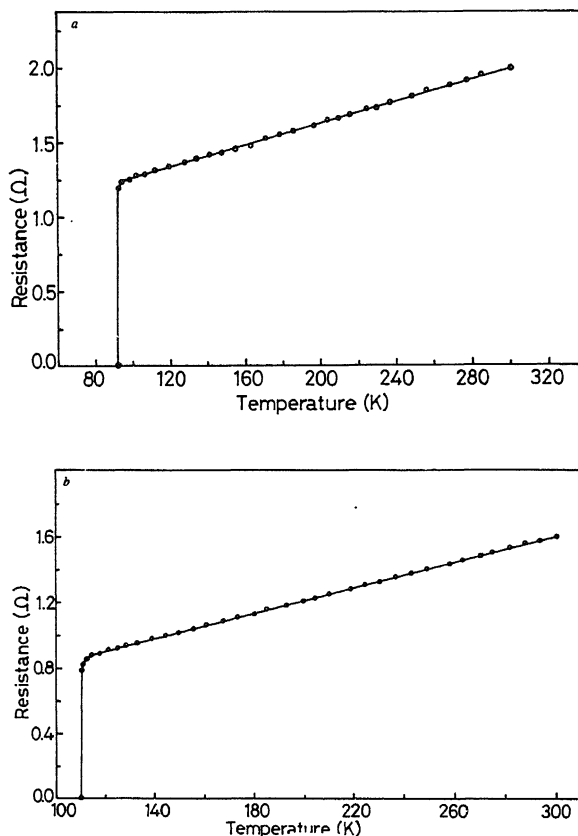


Figure 5. Temperature-resistance curve of screen-printed (a) (b) BiSCCO thick film on YBa₂SnO_{5.5} substrates.

in a range suitable for microwave applications. YBa₂SnO_{5.5} is

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Critical exponent of the electrical conductivity in the para-coherence region of a thin film of YBCO

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Abstract. Critical exponent of the electrical conductivity in the para-coherence region of the high temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) thin film on ZrO_2 substrate prepared by high pressure oxygen ion irradiation was carried out using 100 MeV $^{16}\text{O}^{10+}$ ion irradiation at different temperatures to see the effects of disorder on the value of the critical exponent (γ) changes from a value of about 2 to 1.62 upon irradiation. The effect of ageing and annealing on this film to see the effect of ageing and annealing.

Keywords. High temperature superconductors; resistivity; critical exponent; heavy ion irradiation.

1. Introduction

Excess conductivity studies in the para-coherence region of high temperature superconductors (HTSC) is a subject of interest for the past few years. The superconducting transition is a second order phase transition characterized by a critical temperature T_c which is zero above the transition temperature T_c and goes to infinity below T_c . Large number of studies were performed to study the

for the susceptibility of the 3D XY ferromagnet. This has been calculated to be 1.316 from renormalization group theory (Guillou and Zinn-Justin 1977). It was also shown by the disorder in the strength of the exchange interaction does not change the exponent. If the γ in the conductivity of the granular material is identified with the corresponding exponent in the susceptibility of the ferromagnet, one would expect that the conductivity exponent is also independent of disorder.

We performed experiments on a superconducting thin film of YBCO about 3000 Å with heavy ion irradiation to see if the conductivity is unchanged or it changes with irradiation and subsequent annealing, as reported.

2. Experimental

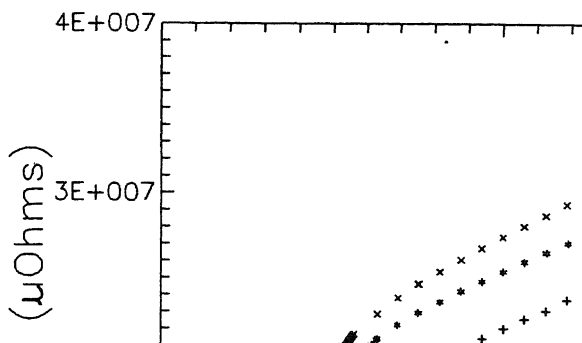
High quality thin film of YBCO was prepared using high vacuum facilities available at the Indian Institute of Science, Bangalore. The film of YBCO was grown on (100) plane of the ZrO_2 substrate. This was confirmed from powder X-ray diffraction pattern using a D/MAX X-ray diffractometer. Figure 1 shows the X-ray diffraction pattern before irradiation. Precise four-probe electrical resistance measurements were carried out using a fully automated electrical resistance measurement system consisting of a closed cycle refrigerator, a Schlumberger nanovoltmeter, a current source and a DRC-93C Lakeshore temperature controller controlled to an accuracy of 10 mK using a calibrated plat-

Critical exponent of electrical conductivity of YBa

Conducting silver paint was used to make ohmic contacts taken for the temperature stability and to correct the effect

The sample was irradiated by 100 MeV oxygen ion beam of 10 MV tandem Pelletron Accelerator (Kanjilal *et al* 1993) at the Centre, New Delhi. It was mounted on a liquid nitrogen cooling scattering chamber in the materials science beamline. The chamber was pumped to a pressure of 1.6×10^{-7} m bar. The temperature of the top surface of the film was about 95 K. The irradiation to a fluence level of 10^{11} particles/cm² was carried out using a beam having a flux of about 10^{11} particles/cm²/s. The sample was held in a secondary electron suppressor geometry. The number of particles falling on the sample was estimated by a combination of a Faraday cup and pulse counter. After irradiation the cold finger got warm and the sample got to room temperature. After 10 h the chamber was vented to atmosphere and filled with dry nitrogen gas.

Resistance measurements were carried out before and after irradiation and after 60 days of irradiation to see the effects of ageing. The

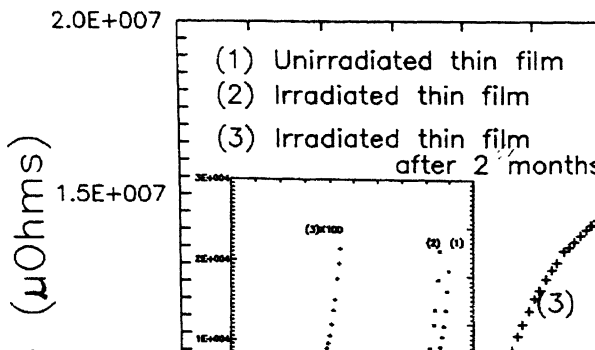


in flowing oxygen at 500°C and once again the measure the effect of annealing.

3. Results

Thickness of the film used was approximately 3000 Å. electronic energy loss as well as the range of oxygen and ZrO_2 substrate were made. For a thick sample of 48 µm. Since the range is more than the thickness of the ions passed through the film and there was no implantation can expect a uniform damage to the sample. The electronic energy loss of a 100 MeV oxygen ion beam in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is 145.7 eV/Å. The power is 0.0828 eV/Å. These are nearly constant over the range of the oxygen ions would have been stopped in ZrO_2 substrate was 300 µm.

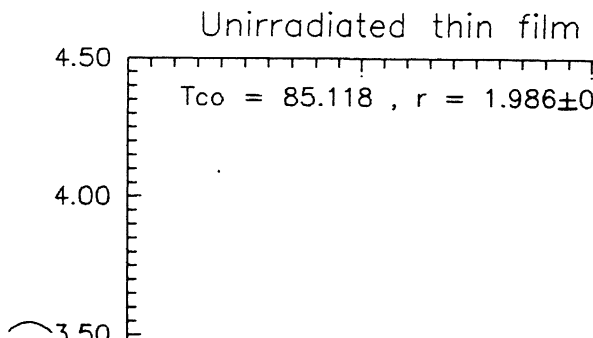
The results of the electrical resistance measurements are shown in figure 2. It is apparent that electrical resistance



Critical exponent of electrical conductivity of YBaC

temperature increased after irradiation. Also the slope (dR/dT) of the irradiated sample than for the unirradiated sample. Such a behavior is observed in samples in which oxygen content is decreased by irradiation induced. Figure 3 shows the resistance vs temperature in the vicinity of the transition temperature. It is clear from this figure that the transition temperature of the irradiated sample is slightly higher than the unirradiated sample.

Data points were taken at every 50 mK interval. Then a plot of $\log(R)$ against $\log(T - T_{co})$ using an approximate value of T_{co} by judging from the resistance went to zero in figure 3, the exact values of γ and T_{co} were obtained by the following procedure. The plot of $\log(R)$ vs $\log(T - T_{co})$ was made in the temperature range of $\sim 1^\circ\text{K}$ above T_{co} . From this plot a linear region is estimated. This is a linear plot whose intercept on the $\log(T - T_{co})$ axis is T_{co} . This T_{co} was slightly different from the T_{co} which was used initially to plot $\log(R)$ vs $\log(T - T_{co})$. This value of T_{co} was again used to get a new plot. This procedure was repeated twice and we found that the value of T_{co} converged very rapidly. Figures 4-6 show the plots of $\log(R)$ vs $\log(T - T_{co})$ for



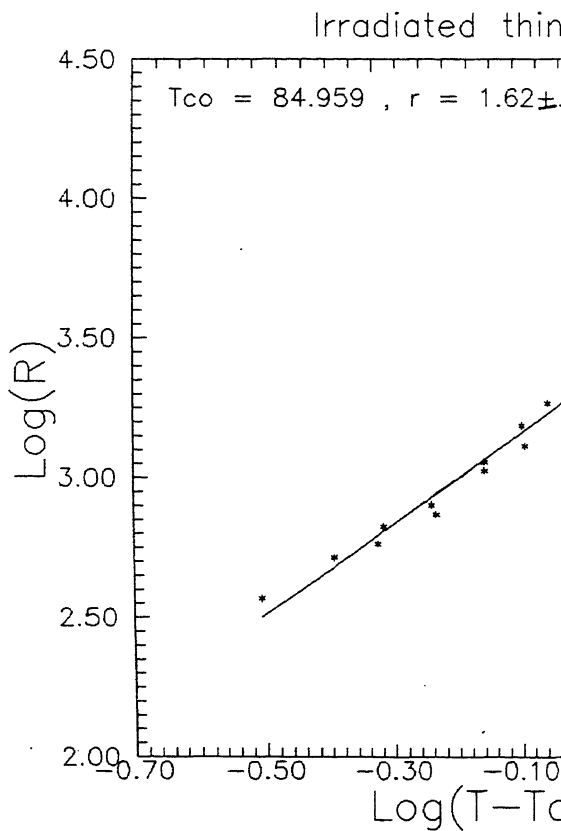


Figure 5. Plot of $\log(R)$ vs $\log(T - T_{co})$ for irradiated samples.

conductivity exponent (γ) changes from its original value

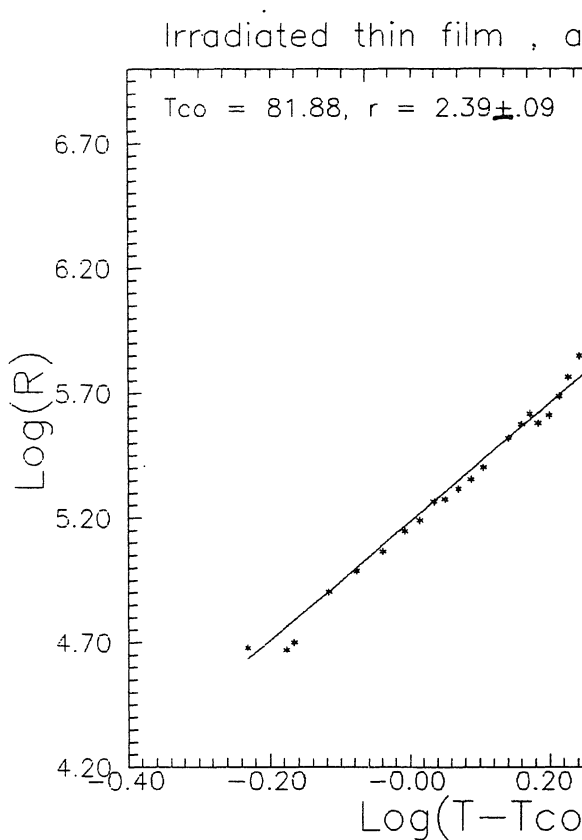
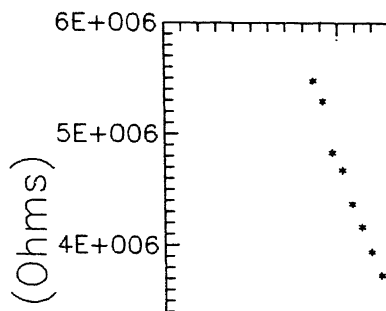


Figure 6. Plot of $\log(R)$ vs $\log(T - T_{co})$ for irradiated sample

superconducting properties. The resistance at room temperature

However it was surprising that T_{co} value decreased upon irradiation. The observed effect of ageing was not expected. However the substantial reduction in the weak links has been reduced probably because the grain boundary has slowly diffused out of the grain followed resulted in further increase in density of the grains.

What was surprising is the large change in T_{co} from 1.99 ± 0.05 to 1.62 ± 0.06 upon irradiation of the tunneling Hamiltonian with 3D X-ray. Then such a large variation in the value of T_{co} in the light of some renormalization group theory of Kaul (1988). Heisenberg model (Lubchanski 1976; Khmel'nitzki 1976; Jug 1983; Weinrib and Lubchanski 1983) site disorder showed that the critical exponent for disorder as long as the specific heat critical exponent is less than one, on the other hand, unconventional renormalization treatment of the critical exponent will depend on frozen disorder is less than zero. However this matter requires further investigation.



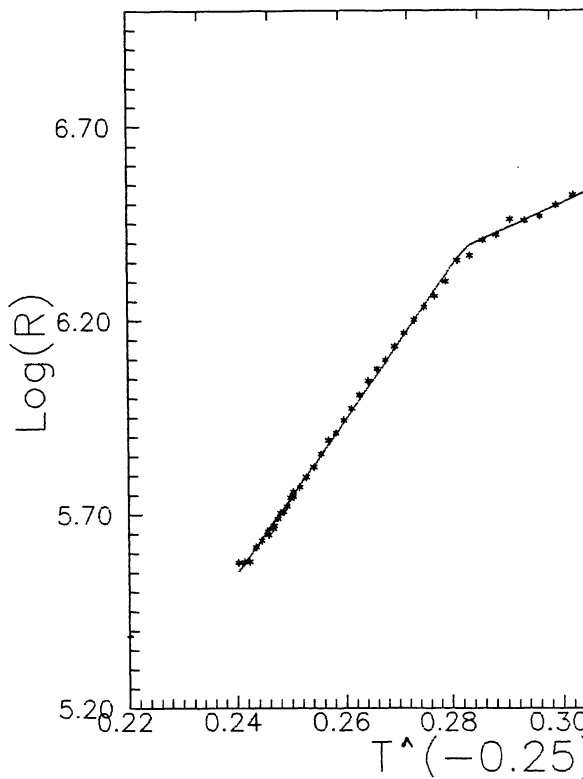


Figure 8. Plot of R vs $T^{-1/4}$ for the semiconducting state after annealing.

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Flux trapping and its effect on AC susceptibility of granular superconductors

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Abstract. Experimental data on the real (χ') and imaginary (χ'') parts of the AC susceptibility as a function of DC bias field (H) shows the effect of flux trapping in high T_c superconductors. The aim was to substantiate our recent proposal on the basis of a two-component critical state model suitable for granular superconductors. Stress has been given to understanding the origin of hysteresis in the data. It was seen in the experimental data that above a certain value of DC field, a new feature appears in $\chi'(H)$ and $\chi''(H)$ creating hysteresis like loops. The calculated loops shows good agreement. $\chi'(H)$ and $\chi''(H)$ show an asymmetry in presence of trapped flux.

Keywords. Susceptibility; superconductors; critical state.

1. Introduction

Understanding the nature of the flux line lattice (FLL) and its interaction with the superconducting ceramics, i.e. granular superconductors, has posed a great challenge to the theoreticians as well as experimental workers. In the last few years, a lot of work has been done in this regard to substantiate our understanding of the phenomenon. Our understanding is far from our reach. The so called phase diagram of the system, which has been accepted for conventional superconductors with a single component, is now looked upon with confusion (Fisher *et al* 1990). The presence of

on field dependence of χ' and χ'' and hysteresis there (Goldfarb and Clark 1985; Nieuwenhuys *et al* 1985; Ciszek *et al* 1991; Lee *et al* 1992), a thorough study in parallel which allows one to exploit the critical state model (Campbell *et al* 1983) because in that case one can calculate quantities and hence a simple one-dimensional critical state model for the purpose. A more involved model has been recently proposed by Saha *et al* (1994). In presence of a DC bias field, one has two processes—firstly, the effect of DC biasing in modifying the variation of χ' and χ'' as a function of DC bias field and secondly, the reorganization within a given AC cycle and consequent loops—major $M-H$ loops due to DC biasing and superposition of minor loops due to AC field at different DC bias fields. In order to compare with experimental data any model calculation must handle the situation by considering the experimental situation in detail, i.e. how the AC field is being imposed. There may be two situations, viz. (i) the AC field is being imposed while the DC field is being ramped and (ii) the AC field is being imposed coming to a certain value of the DC field where measurement is being made. It may appear that this does not make much difference. But it brings out the difference in the two cases. If the AC amplitude is small and the step size of the DC field variation then in both cases the resulting loop (i.e. the DC profile modified by the AC oscillation) and hence the loop will be nearly the same. But if the step is large then in the second case the major loop will be disturbed by the AC field of measurement only and hence the two cases will be different. Saha and Das (1993b) model calculation resembles the latter case and hence at lower amplitude additional hysteresis can be observed after correction and which usually are not seen in the data of Campbell *et al* (Goldfarb and Clark 1985).

Flux trapping and its effect on granular supercon

case, i.e. AC field was continuously on. In absence of a b not possible to have exact balance at a given frequency. the non-uniformity in the primary field one could achieve by moving the secondary pairs within the primary. The offsetted by using the built-in facility of LIA or through bring out possible significance from these arbitrary measure offsetted at the highest DC bias field and then plotted.

3. Model calculations

The method of calculation is described elsewhere and will (Saha and Das 1993b). To bring out better fit to the data bias field is kept quite less (0.01 mT) during model calculation. resemblance with experimental situation and hence the calculation should not be confused with that of Saha and Das (1993) was 0.1 or 2.0 mT. Further, as we shall consider the low not consider demagnetization contribution due to grains. In basic nature of data we consider a higher bulk demagnetization of 0.3 as considered in Saha and Das (1993b).

4. Results and discussion

4.1 Range effect of DC bias field

In figures 1a and b the real (χ') and imaginary (χ'') parts a function of DC bias field have been plotted for a p amplitude of AC excitation was 0.3 mT, the highest amplitude work. In interpreting these results it has to be remembered

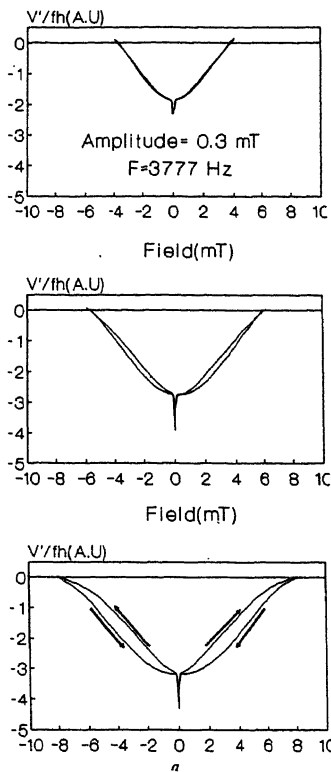


Figure 1. a. $V'/fh (\approx \chi')$ as a function of field and b. $V''/fh (\approx \chi'')$ as a function of field.

$$dH_c/dt \ll H \omega_c$$

Flux trapping and its effect on granular superconductors

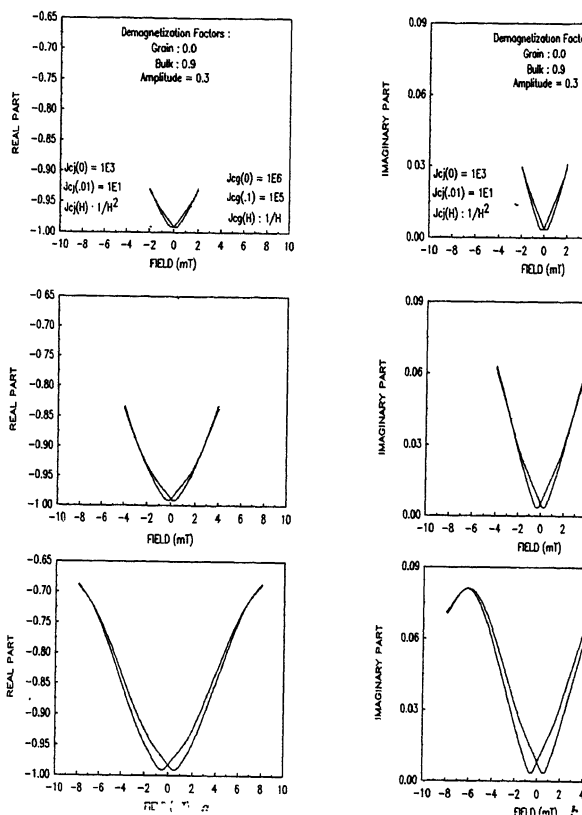


Figure 2. a. Calculated $\chi'(H)$ for three DC bias ranges with J_{cj} parameters (in A/cm²) and their field dependence as shown in Figure 1. b. Calculated $\chi''(H)$ for three different DC bias ranges with parameters of a.

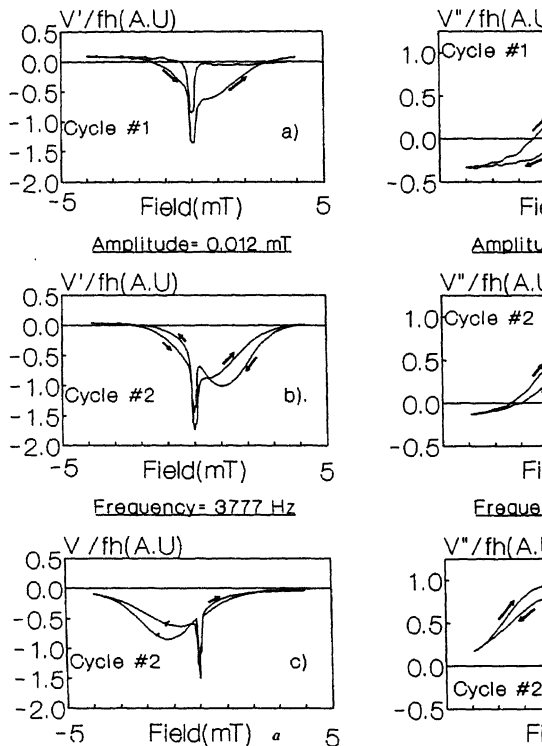


Figure 3. a. V'/fh as a function of DC bias field after V''/fh as a function of DC bias field after applying a t

the basis of the model calculations as given by Saha calculation has been reproduced in figure 2 with inter

Flux trapping and its effect on granular superconductor

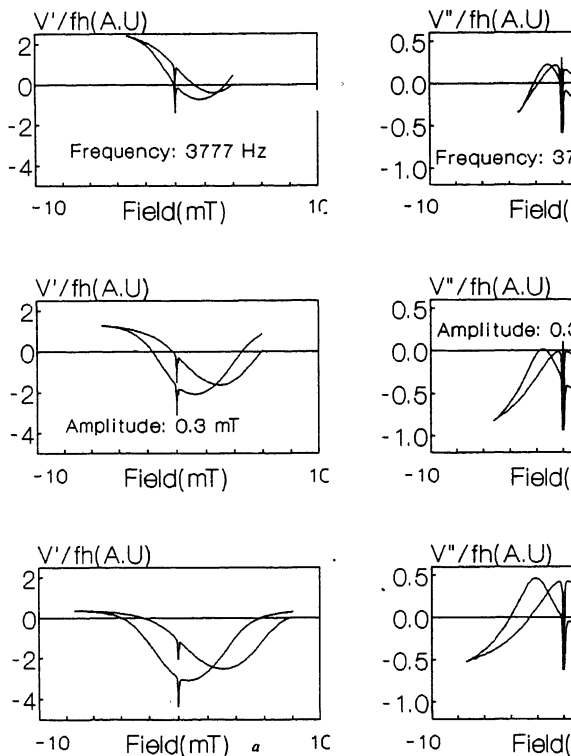


Figure 4. a. V'/fh as a function of DC bias field for different frequencies and b. V''/fh as a function of DC bias field for different amplitudes.

trapped which distorts the symmetry of the loops (curve b). That this asymmetry is certainly due to the trapped flux can be

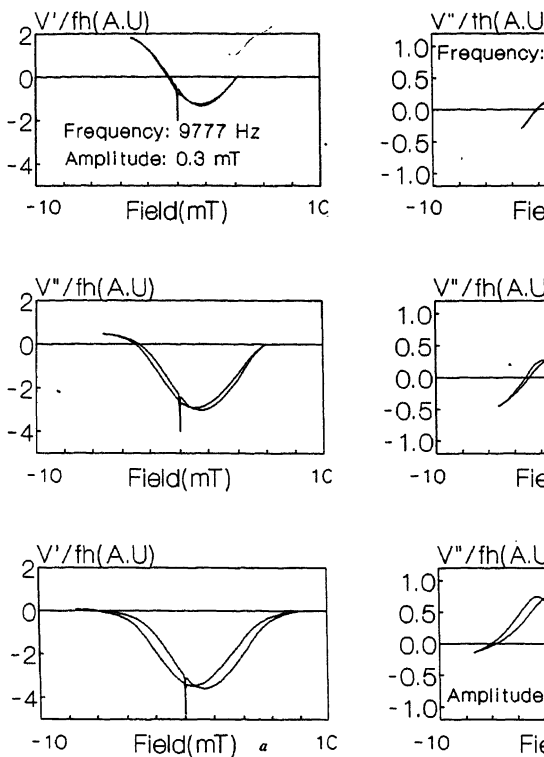
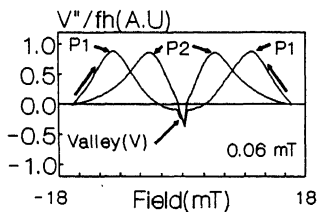
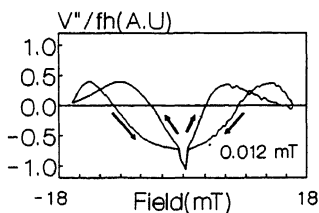
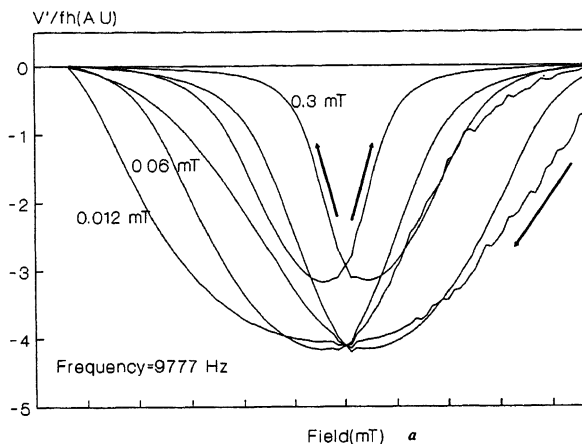


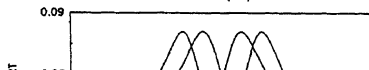
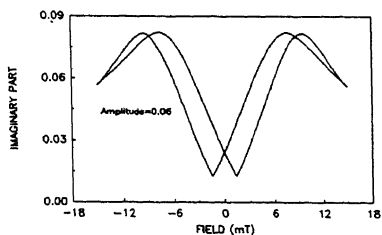
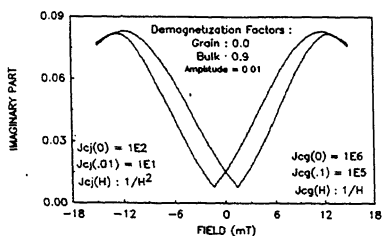
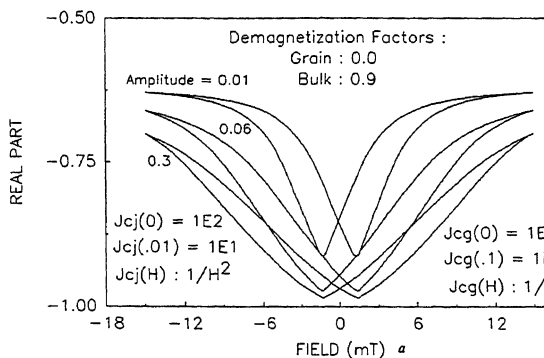
Figure 5. a. V'/fh as a function of DC bias field for c #2) and b. V''/fh as a function of DC bias field for different

4.2 Amplitude dependence of the $\chi'(H)$ and $\chi''(H)$ loops

The dependence of χ' and χ'' loops on amplitude of

Flux trapping and its effect on granular superconductors





Flux trapping and its effect on granular superconduct

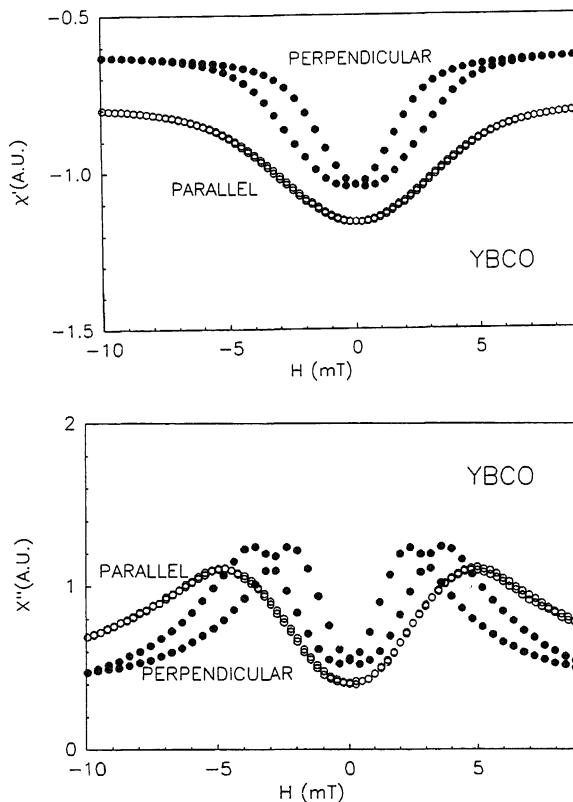


Figure 8. Measured $\chi'(H)$ and $\chi''(H)$ of a YBCO sample with the magnetic field applied parallel or perpendicular. Note the increase in hysteresis in perpendicular.

However, the obvious disagreement with the model calculations could not reproduce the amount of hysteresis in experimentally. The obvious limitation of the model is that it is one-dimensional and cannot account for the curved flux lines inside the

5. Conclusions

Dependence of AC magnetic susceptibility on the superimposed DC bias field for granular high T_c superconductors shows considerable variation with increasing bias fields. The shape of the curves depends on the intensity of the current densities, the demagnetization factors of the grains, the orientation of the AC and DC fields. Trapped flux, in addition to the shape of the $\chi'(H)$ and $\chi''(H)$ curves. Therefore, extreme care is required while interpreting the susceptibility data to arrive at a two-component critical state model can explain general $\chi''(H)$ curves, but a quantitative match between the experimental data and predictions can only be possible when more intricate models are developed.

Acknowledgements

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History effects in low-field magnetoresistance of BPSSCO polycrystals

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Abstract. Low-field ($H < 40$ G) magnetoresistance measurements on $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ polycrystals at several temperatures show considerable hysteresis in $\rho(H)$. In a zero-field-cooled state, the field is increased from 0 to a maximum value and then lowered. The observation of hysteresis is taken as an evidence for field-induced superconductivity. The data show that the hysteresis in $\rho(H)$ occurs for applied fields much less than H_c . $d\rho(H)/dH$ exhibits a discontinuity. In addition, we find that the effective intergrain field (H_a) is lowered from a maximum field, the effective intergrain field is zero for $H_a > 0$, which gives rise to a minimum in $\rho(H)$.

Keywords. Magnetoresistance; hysteresis; high- T_c superconductors.

1. Introduction

Polycrystalline samples of high-temperature superconductors have been recognized as granular superconductors. They consist of grains coupled by weak links. The current induced dissipation in the sample is governed by the presence of two types of current, viz. the intergrain current and the intragrain current. The low value of bulk J_c measured in polycrystals and its reduction by about two orders of magnitude in low fields have been described by a model describing Josephson type of coupling (Paterson and Eliot 1988).

We report here low-field magnetoresistance measurement on a $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ sample at various temperatures. A linear $R(H)$ exists at fields far below the peak in $dR(H_a)/dH_a$ and penetrates into the grains at a field much lower than is reported by Lopez *et al* (1992).

2. Experimental

Samples in the form of pellets of nominal composition were prepared in the standard ceramic route. For resistance measurements, samples used were of dimension $10 \times 1.1 \times 1.49$ mm. Four probe contacts were made of Indium solder and the contact resistance was $< 5 \Omega$. A current of 1 mA at 23.1 Hz was passed through the sample. The voltage was measured with a lock-in amplifier (SRS 530) with a low noise transformer at the input stage. The temperature was measured by a Pt-100 sensor driven by a 1 mA dc current from a constant current source (sensed by a DMM (Keithley 196). Temperature was controlled within ± 0.05 K at each temperature.

3. Results and discussion

The resistivity at room temperature of the sample is $\rho \approx 2.5$ m Ω . The variation of resistivity, ρ as a function of temperature is shown in Fig. 1. The variation is linear in T above $T_c(\text{on}) \approx 120$ K. Between $T_c(\text{on})$ and $T_c(\text{zero})$ the decrease in ρ is fairly sharp. Below 105 K the fall in ρ finally achieve a $T_c(\text{zero})$ at 98 K. Similar tails in $\rho(T)$ are observed in other

in other BSCCO granular materials and is likely a result of grain-grain coupling. The fall in ρ between 113 and 105 K is associated with superconductivity within the grains. Between 105 and 98 K the fall is due to phase incoherence between the grains, and below 98 K the resistivity is zero. In. There appears a distinct change in $\rho(T)$ at 105 K. $\rho(105 \text{ K}) = 458 \mu\Omega \text{ cm}$, i.e. $\rho(105 \text{ K}) < \rho(0 \text{ K})$ (extrapolated) $\approx 1.19 \text{ m}\Omega \text{ cm}$. $\rho \geq 458 \mu\Omega \text{ cm}$ is identified with the ρ of decoupled grains.

In figures 2-7 the variation of ρ as a function of applied field is shown for temperature $T = 81.5, 85, 90, 95, 100$, and 105 K , respectively. All samples are zero-field-cooled at each temperature, and then the field is increased ($H^\uparrow$) mode and in the field decreasing ($H_\downarrow$) mode. The field, $H_m = 38 \text{ G}$. Pronounced hysteresis is observed between the field increasing and decreasing measured temperatures. The value of magnetoresistivity $\Delta\rho(H)$ at a given field increases as the temperature is increased up to 105 K .

At $T = 81.5$ (figure 2) magnetoresistance is observed beyond H_m . In $H^\uparrow$ mode the nature of the curve is such that the derivative $d\rho/dH$ increases and no discontinuity is observed. When the field is lowered to 38 G , it is observed that $\rho(H_\downarrow) < \rho(H^\uparrow)$. It is also found that for $H_a < 12 \text{ G}$, $\rho(H_\downarrow) = \rho(H^\uparrow) = 0$. For $T = 85 \text{ K}$ (figure 3) $\rho(H)$ is similar to that at $T = 81.5 \text{ K}$ except for $H_1^\uparrow = H_{1\downarrow} = 0$.

At $T = 90 \text{ K}$ (figure 4) the behaviour of $\rho(H)$ departs from the previous ones. Here $H_1^\uparrow = 3.5 \text{ G}$ beyond which ρ increases rapidly and the rate of rise in $\rho(H)$ decreases, i.e. $d\rho(H)/dH_a$ undergoes a minimum. The resistivity at H_2 corresponds to $36 \mu\Omega \text{ cm}$. On lowering the field $\rho(H_\downarrow) < \rho(H^\uparrow)$ till H_3 , below which $\rho(H_\downarrow) > \rho(H^\uparrow)$. In addition $\rho(H_\downarrow)$ is lowered to 0. This may be termed as the remanent magnetization to remanent magnetization.

At $T = 95 \text{ K}$ (figure 5), $H_1^\uparrow \approx 2 \text{ G}$, the field $H_2^\uparrow$ occurs at 6 G . On increase of field ρ falls rapidly and field dependence appears to be similar. On lowering H_a from H_m , H_3 is found to shift to higher field and the minimum in $\rho(H)$ is observed for $H_a \approx 2$ below which the

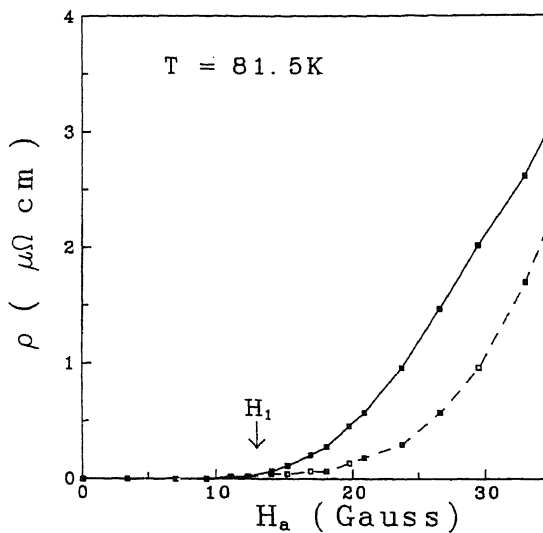
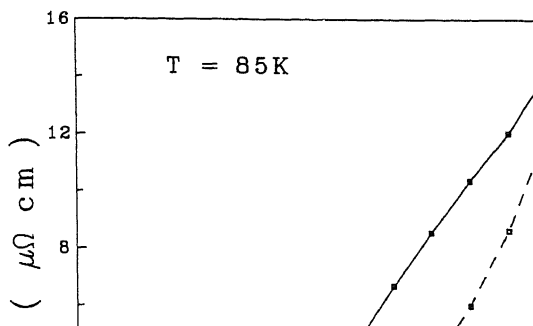


Figure 2. For caption, see p 612



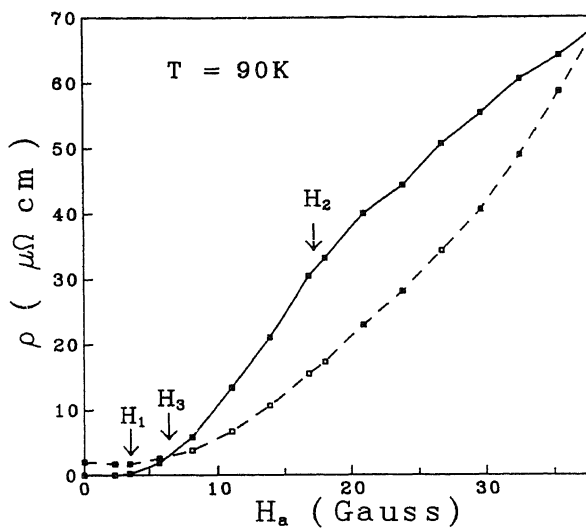
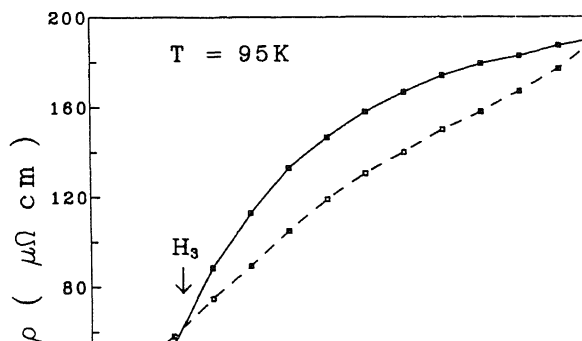


Figure 4. For caption, see p. 612.



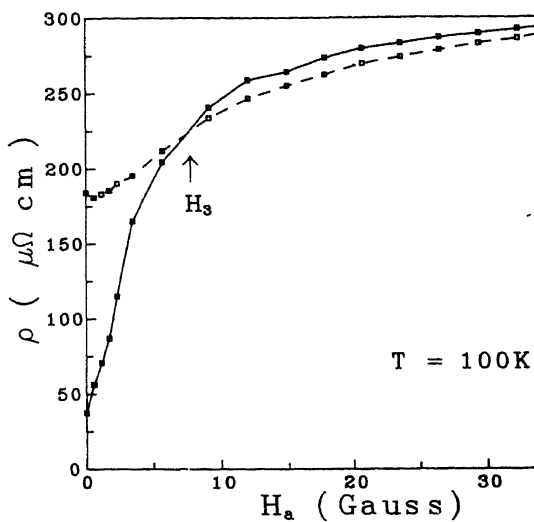
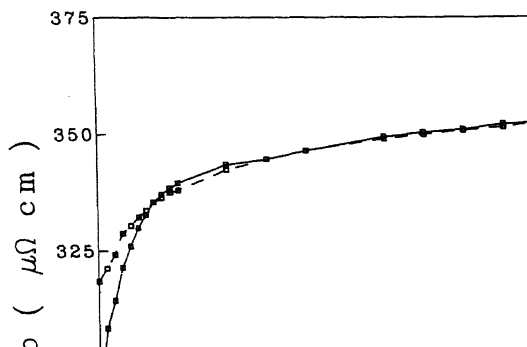


Figure 6.



Effect of oxide additives on T_c behaviour of $\text{Bi}_{2.1}\text{Sr}_{1.93}\text{Ca}_{0.97}\text{Cu}_2\text{O}_8$ system*

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Abstract. We have carried out studies on the effect of oxide additives ($\text{Ca}_{0.85}\text{Sr}_{0.15}\text{CuO}_2$, BaBiO_3 and BaPbO_3) on Bi-2212. Compositional additives have been prepared and characterized by XRD, resistivity and susceptibility techniques. XRD studies indicate that all the materials are single phase. Susceptibility studies indicate enhanced granular behaviour with increasing temperature (400°) sintering results in degradation of the T_c of the additives.

Keywords. Oxide additives; T_c behaviour; BiSrCaCuO .

1. Introduction

The high T_c materials are generally granular in nature with grain boundaries between the grains (Camps *et al* 1987). This is one of the major obstacles in achieving high J_c (Ekin *et al* 1987; Cizek *et al* 1988; Kirtley *et al* 1988). The susceptibility technique has proved to be very useful in studying the granular nature of these materials. In the Bi-2212 system, the technique indicates the contributions from the individual grains (intragrain) and grain links (intergranular) to the diamagnetic signal. The weak link nature of these materials, reasons such as compositional non-stoichiometry, intergrowth, impurities etc. It is interesting to study the effect of additives on the T_c as well as the microstructure of these materials. The additives

and CaCO_3 (99.98%; all Cerac, UK), were and calcined in air at 810°C for 16 h. The carried out in air at 840°C for 5–6 h and 8. The material was then pressed into pellets (mm) and sintered at 870°C for 10 h in air. In order to enhance the T_c , the samples at 805°C for 1–2 h and then quenched. BaBiO_3 and BaPbO_3 were added in steps of Bi-2212. The mixture was ground thoroughly, the resulting powder was pressed into pellets and sintered for 24 h.

The samples were characterized by powder XRD. Resistivity measurements were carried out in the temperature range 300–13 K using a four-probe method (Keithley 642, Cleveland, Hareas, Germany). AC susceptibility measurements were carried out in a field of 0.1 Oe and frequency of 300 Hz using a SQUID magnetometer (MPMS-20, the Sumitomo superconducting properties laboratory, 204-T, Japan). The microstructure was studied by scanning electron microscope (SEM; JEOL unit).

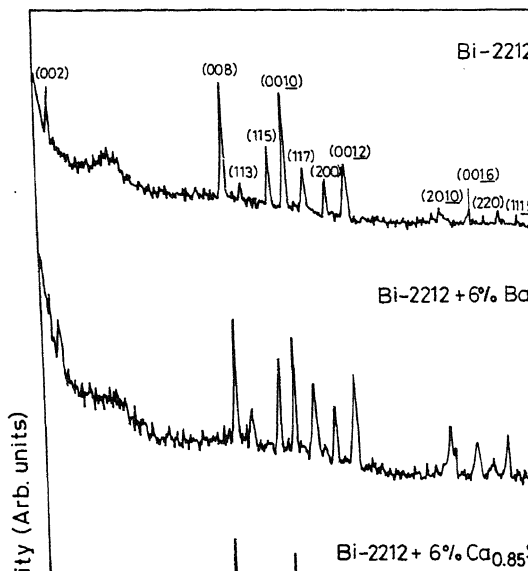
3. Results

XRD studies indicate that all the compositions form a single phase (figure 1). Sharp peaks are observed, indicating the nature of the phases. The XRD patterns are indexed to the orthorhombic Bi-2212 structure and no other phases are observed. Lattice parameters have been calculated using the Bragg reflections (table 1). The a and b lattice parameters change while the c -lattice parameter increases with the concentration of BaBiO_3 and BaPbO_3 added. Bi-2212 showed metallic behaviour in all the samples. The ρ and ρ/T vs. T plots for

oxide additive containing phases of Bi-2212.

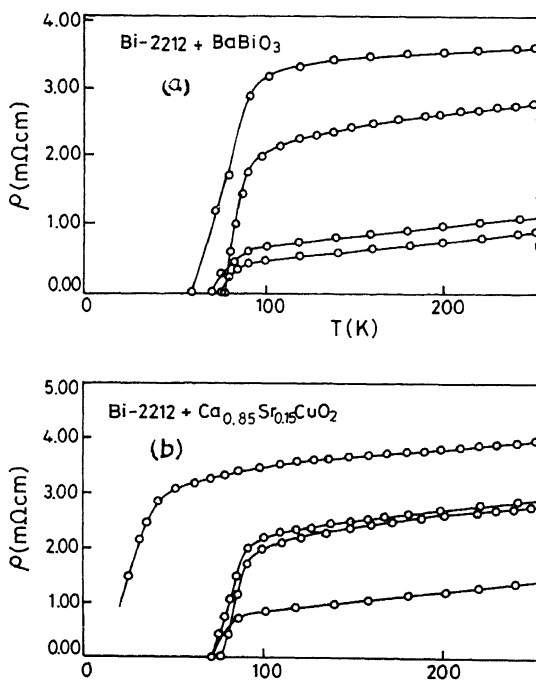
ΔT_c (K)	ρ_{300} m Ω cm	ρ_0 m Ω cm	α $\mu\Omega$ cm/ $^{\circ}$ C	Susceptibility data				
				χ'		χ''		
				$T_{c, \text{gran}}$ (K)	$T_{c, \text{bulk}}$ (K)	δT_c^a (K)	$T_{c, \text{peak}}$ (K)	FWHM ^b (K)
14	2.7	1.4	4.3	90	82	8	80	6
18	2.8	1.7	4.3	80	69	11	68	8
11	1.6	0.5	3.6	77.5	66	11.5	62	6.4
—	4.0	3.2	3.2	76.6	58.5	18	50	15
10	1.0	0.2	2.6	75	69	6	68	6
17	1.2	0.3	2.6	82.5	70.5	12	66	8.5
30	3.7	3.2	2.4	82	49	33	38.5	16
13	1.5	0.5	3.3	79	69	10	67	6.4
—	—	—	—	79	68	11	65.5	6.5
12	1.7	0.75	3.2	79	68.5	10.5	65	6.4

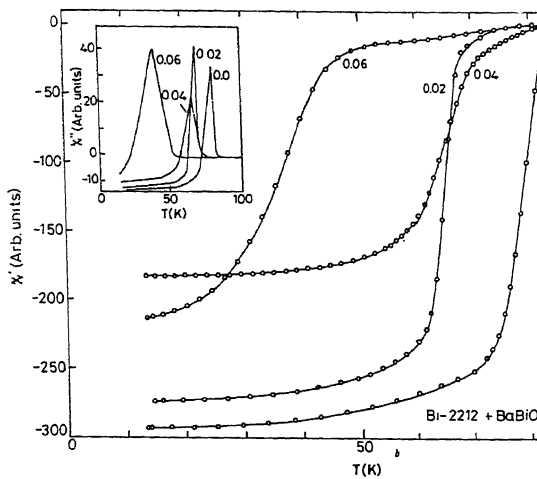
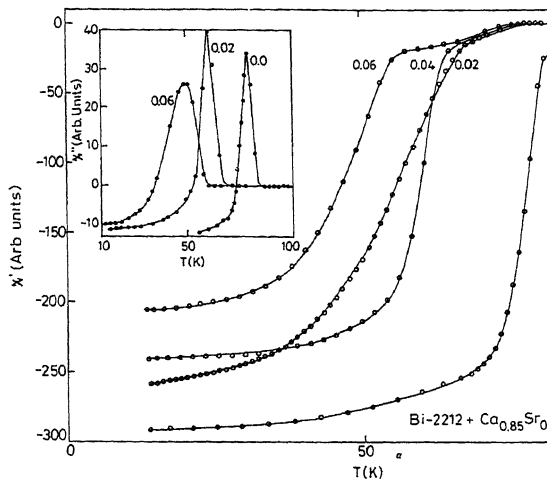
Consistent $T_{c, \text{zero}}$ values in the range 74–76 K were obtained in the pure Bi-2212 compound. AC susceptibility studies on the pure Bi-2212 compound show a characteristic behaviour which reflects the transition from the regime where the grains are decoupled ($T_{c, \text{gran}}$) to the regime where the intergrain coupling becomes dominant for the whole sample ($T_{c, \text{bulk}}$). In the compounds containing additional BaO, similar observations have been made. (i) Resistivity studies indicate that with increasing additive concentration, the superconducting transition temperature T_c systematically decreases and the ΔT_c ($T_c(90\%) - T_c(10\%)$) increases, as can be seen from table 2 and figure 2 (a,b,c). However, in Bi-2212 + BaPbO₃, although $T_{c, \text{zero}}$ decreases with concentration, (ii) from the plot of the real part ($\chi' - T$) of the ac susceptibility, both $T_{c, \text{gran}}$ and $T_{c, \text{bulk}}$ register a decrease in the additive concentration.



Effect of oxide additives on T_c behaviour of BiSrCa

the pure Bi-2212. However, variation in $T_{c, \text{gran}}$ is not significant as the concentration increases from 2 to 6 mole%. On the other hand, $T_{c, \text{bulk}}$ decreases systematically with increasing additive concentration from 2 to 6 mole% for compositions containing BaPbO_3 . Effectively, the temperature difference ($T_{c, \text{gran}} - T_{c, \text{bulk}}$ denoted by δT_c) increases (table 2) from 10 K to 15–20 K for the samples containing additives. For the samples containing BaPbO_3 , a decrease in both $T_{c, \text{gran}}$ and $T_{c, \text{bulk}}$ are observed and





same for all concentrations of the additives and (iii) the χ' concentrations of additives (insets of figures 3a, b and c) in of the $\chi''-T$ peak increases with increasing concentration of in the case of BaPbO₃.

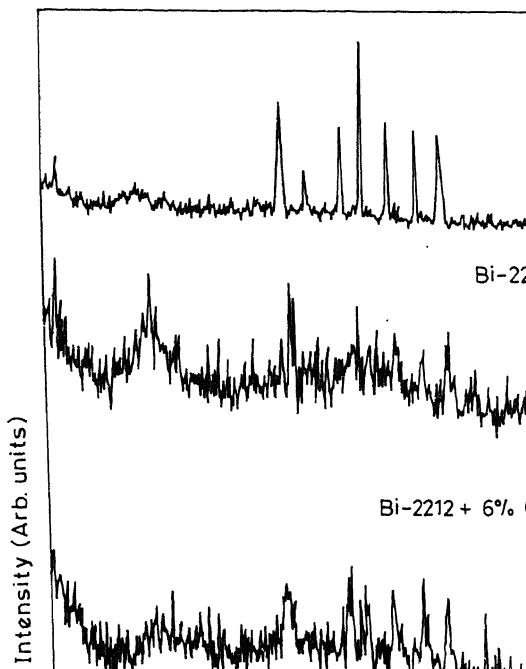
4. Discussion

The difference $T_{c, \text{gran}} - T_{c, \text{bulk}}$ (δT_c) represents the extent of gran The material can be thought of as consisting of a large number in a matrix of inhomogenous phase (grain boundary) which between the grains. For very low ac fields, the nature and weak link network relative to that of the grains determines t high value of δT_c observed for the compounds cont Ca_{0.85}Sr_{0.15}CuO₂, indicates that the added oxide phases segregat leading to an increase in the transition width. In other words, between the grains decreases and bulk superconductivity ($T_{c, b}$ temperature. In the compound with 6 mole% of Ca_{0.85}Sr_{0.15}C signal does not saturate down to the lowest temperature. This is with the $\rho - T$ data where a drop in the resistivity is observed bu is detected down to 13 K. The materials containing BaPbO show any increase in δT_c in the $\chi'-T$ plot. This is in agreee obtained from resistivity measurements (figure 2c) where Δ constant. The additives do not become superconducting on effect. In case the additives were to become superconduct decreased which is not so in the present case.

A single sharp peak in the $\chi''-T$ plots indicates the exc material with good coupling between the grains. If r_g is the grains and λ the London penetration depth, then for $r_g \gg \lambda$ very sharp for low values of h_0 (Senoussi *et al* 1991). For v areacovered by the weak link network is negligible. This is T_c approaches T_c (or $h_0 \rightarrow 0$) λ^2 and λ^2 is directly proportional to

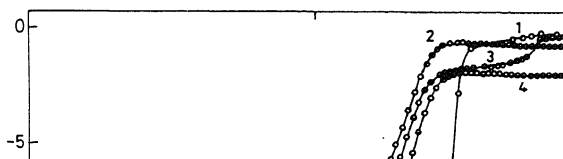
BaPbO_3 , the width of χ'' is almost a constant indicating change in the microstructure which is clearly in agreement from resistivity data.

Scanning electron microscopy (SEM) photographs show the microstructure of the pure and additive compositions. Correlations were not possible with the observed superconductivity.



5. Effect of low temperature sintering

To explain the enhanced granular behaviour in the above phases two possibilities: (i) the added oxides are non-interactive and the grain boundary region, as described earlier, since XRD proves that the materials are all single phase and no impurities were observed and (ii) since the sintering temperature is as high as the interaction of the added oxide material with Bi-2212 cannot be observed and may be within the limits of detection by XRD. This could be due to decomposition of the Bi-2212 superconductor and hence bulk superconductivity is observed at much lower temperatures. It was thought that at lower temperatures (say 400°C) the interaction of the additive phase would be minimal. We therefore prepared the end compounds of BaBiO_3 , BaPbO_3 and $\text{Ca}_{0.85}\text{Sr}_{0.15}\text{CuO}_2$. The heat treatment was done on powder at 400°C for 3 days; pelletized and sintered at 400°C . A Bi-2212 pellet was also heated at the same temperature. XRD confirmed that the material was found to be single phase and remained unchanged when containing additives showed very broad and less intense peaks. To check its reproducibility, we repeated the experiment and obtained similar results. AC susceptibility studies on these phases are shown in figure 5. For the samples containing BaBiO_3 and BaPbO_3 , the $\chi'-T$ plot shows a drop around T_c in the presence of a small amount of high T_c (Bi-2223) phase.



occurs at a much lower temperature. For the $\text{Ca}_{0.85}\text{Sr}_{0.15}\text{CuO}_2$, the high T_c phase is not seen. As can be seen in all the three cases has considerably decreased and the peak is broad. This indicates that the additive essentially degrades the high T_c phase. This favours the formation of the high T_c phase at 400°C . However, the presence of Bi-2223 could be seen in the XRD patterns since it has been well-crystallized when heated at such low temperature. The melting temperature of Bi-2223 is 858°C which is lower than that of Bi-2212, hence it appears that in the presence of additives, the materials melt when heated at low temperatures leading to the slow degradation of the high T_c phase. The photographs taken on all these materials indicate qualitative changes in the microstructure of the compounds with additives.

6. Conclusions

Studies on the effect of oxide additives on $\text{Bi}_{2.1}\text{Sr}_{1.93}\text{Cu}_2\text{O}_{10}$ show a change in the granular nature. Single phase materials were obtained with 6 mole% of the additives showing that the additives are effective. The $(\rho-T)$ and ac susceptibility $(\chi-T)$ studies indicate that the T_c increases, viz. BaBiO_3 and $\text{Ca}_{0.85}\text{Sr}_{0.15}\text{CuO}_2$ progressively increase $(T_{c,\text{gran}} - T_{c,\text{bulk}})$ with increasing concentration. SEM studies show changes in the microstructure. No significant changes in the compositions with BaPbO_3 .

Low temperature sintering of the compounds containing additives indicate that the materials are almost amorphous when heated at 400°C . Bi-2212. AC susceptibility studies show that Bi-2212 is not stable in the presence of the additives when heated at low temperatures (400°C) leading to the degradation of the high T_c phase.

Acknowledgement

Growth and characterization of laser-deposited Ag-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin films on bare sapphire

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Abstract. Microstructural and superconducting properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin films deposited *in situ* on bare sapphire by pulsed laser deposition using $\text{YBa}_2\text{Cu}_3\text{O}_7$ and 10 wt% Ag have been studied. Ag-doped films grown at 77 K have shown very significant improvement over the undoped $\text{YBa}_2\text{Cu}_3\text{O}_7$ films grown at identical condition. A zero resistance temperature of 90 K and a critical current density of $1.2 \times 10^6 \text{ A/cm}^2$ at 77 K have been achieved on bare sapphire for the Ag-doped films. The improved connectivity among grains and reduced reaction rate between the grains caused due to Ag in the film are suggested to be responsible for the improved transport properties.

Keywords. Pulsed laser deposition; Ag-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin films; critical current density; sapphire.

1. Introduction

Thin films of high temperature superconductors are highly useful in electronic and microwave circuits due to their high critical current density and low surface resistance at liquid nitrogen temperature. Excellent films with critical current density higher than 10^6 A/cm^2 and microwave surface resistance less than $300 \mu \text{ ohm}$ at 77 K are now routinely prepared on lattice matched substrates such as SrTiO_3 and LaAlO_3 by pulsed laser deposition (PLD) technique.

It was in this context that we thought that the significant benefit in bulk (Tiefel *et al* 1989; Ju *et al* 1991) films (Singh *et al* 1992; Kumar *et al* 1993; Pint *et al* 1993) may be beneficial in depositing the film at low temperature. Temperature is the most crucial parameter which affects the chemical reaction between the YBCO film and the substrate (Kumar *et al* 1990). In this paper, we report the *c*-axis oriented films on bare sapphire by pulsed laser deposition. The main feature of our results lies in the realization of good quality films at low temperatures with the aid of Ag-doping.

2. Experimental

Undoped and Ag-doped YBCO films were grown on sapphire substrates by pulsed laser deposition technique. A KrF excimer laser was used for ablation. The target-substrate distance was 10 mm, pressure was 300 mTorr. The films were cooled in the growth chamber itself after the termination of the laser pulse. The same as reported earlier (Hegde *et al* 1993). In this work, the targets were prepared by adding 7 and 10 wt% Ag to the YBCO by repelletizing and sintering at 850°C. The films were characterized by resistance, X-ray diffraction (XRD), energy dispersive X-ray (EDX), scanning electron microscopy (SEM). The film thickness measured by profilometer was in the range of 1500–2000 Å. The thickness uniformity was found to be within $\pm 5\%$.

3. Results and discussion

3.1 Transport properties

Growth and characterization of YBaCuO thin films

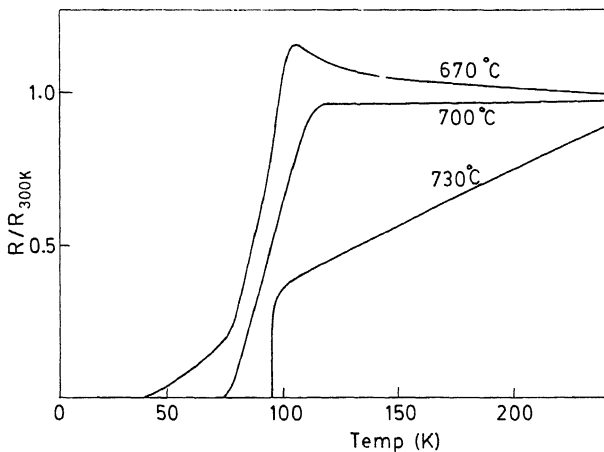
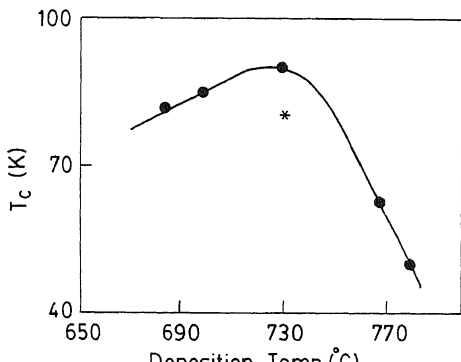


Figure 1. R vs T plots of Ag-doped YBCO films grown on (100) substrates at different temperatures



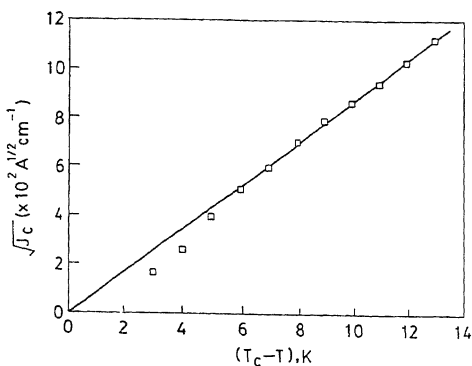


Figure 3. $\sqrt{J_c}$ vs $(T_c - T)$ for Ag-doped film grown at

77 K. Figure 3 shows the plot of $\sqrt{J_c}$ vs $(T_c - T)$ of a Ag-doped film grown at 730°C. The linear variation of $\sqrt{J_c}$ with $(T_c - T)$ is characteristic of a superconductor-normal metal-superconductor (S-N-S) junction. This is in agreement with the model proposed by De Gennes (1969) according to the following expression:

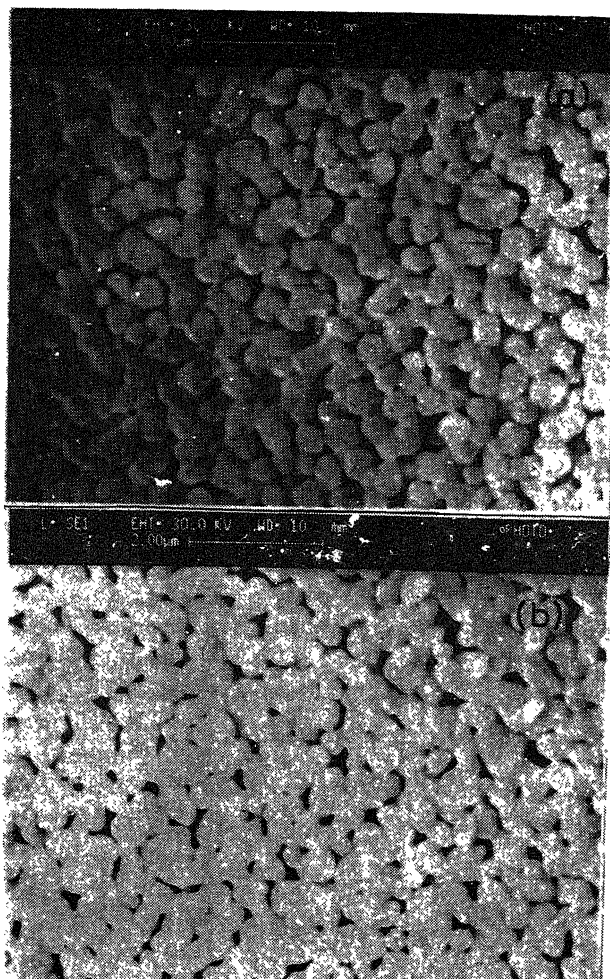
$$J_c \propto (T_c - T)^2 \exp(-d/\xi_n),$$

where d is the thickness of the grain boundary layer in the normal metal grain boundary. If we ignore the variation of ξ_n as compared to $(T_c - T)^2$ term, we can write

$$\sqrt{J_c} \propto (T_c - T) \exp(-d/2\xi_n),$$

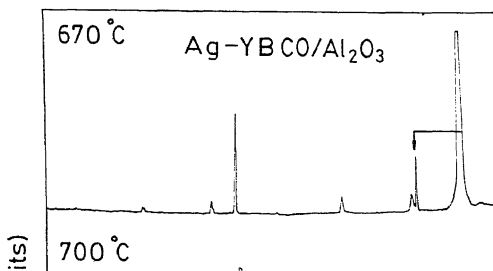
where $\exp(-d/2\xi_n)$ term would determine the slope of the line. It is evident that doping of Ag makes the grain boundary a barrier to the flow of supercurrents.

Growth and characterization of YBaCuO thin films



1994). According to this effect, the normal grain growth is retarded when the average grain diameter is two or three times the critical grain size. The stagnation of normal grain growth in film is attributed to free energy barrier in the grain boundary region. At the point of stagnation, the grain boundary and their boundary completely traverses the thickness of the film, leading to the formation of films with relatively large number of voids and smaller grains. The grains in Ag-doped film is however, bigger and more uniform due to secondary grain growth in presence of Ag. The EDX mapping in spot mode on grains and grain boundary regions shows the presence of Ag and Ag had segregated in intergranular regions. The secondary grain growth in the grain boundary regions results in improved connectivity and consequently in the realization of high J_c . The SNS transition temperature established in previous section also suggest this view.

The XRD patterns of Ag-doped YBCO films grown at temperatures of 670–730°C are depicted in figure 5. All the films are c -axis oriented. The relative intensity of most of the $\langle 001 \rangle$ lines of Ag-doped YBCO films at lower temperatures is not only lesser, the full width at half maximum (FWHM) of these lines are also significantly wider as compared to those of YBCO films grown at higher temperatures. This very well explains why the films grown at lower temperatures are having poorer transport properties as discussed



Growth and characterization of YBaCuO thin films

The realization of good quality YBCO films doped with Ag is due to the significant reduction in the chemical attack of the film at relatively low deposition temperatures. The deposition of YBCO at low temperatures without suffering from the problems of orientation and phase formation is feasible in presence of silver due to following mechanisms. The first mechanism, as suggested earlier (Kumar *et al* 1993), involves the release of nascent oxygen to the lattice right during its growth. Silver is in elemental state in the Ag-doped YBCO targets after sintering but gets oxidized in the plume after ablation. These oxidized Ag-species get reduced when it arrives at the substrate surface and provides nascent oxygen to the YBCO lattice. The availability of active oxygen reduces the required deposition temperatures for the formation of YBCO lattice. In other words, it provides active oxygen by Ag atoms to the growing lattice of YBCO to stabilize the orthorhombic phase with right amount of oxygen directly at a temperature of 730°C.

The second mechanism is based on the transfer of momentum from Ag-atoms to other species forming the YBCO lattice. This helps the species to acquire sufficient energy to grow *c*-axis oriented with good quality at relatively low deposition temperatures. In other words, the presence of high velocity Ag atoms substitutes kinetic energy for conventional thermal energy and contributes to the deposition of YBCO films with good quality at relatively reduced temperatures. The third mechanism is based on the catalytic behaviour of Ag atoms which facilitates material transport by providing a liquid-phase kind of environment and accelerates the formation of YBCO lattice. The accelerated growth, as observed in bulk Ag-YBCO composite also (Wu *et al* 1993), helps in reducing the possibility of any reaction that can take place between the plume and the substrate.

4. Conclusion

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Effect of alloying additions on K_{ISCC} of strength NiSiCr steel

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Abstract. The effect of alloying additions viz. cobalt, molybdenum, and the combination of cobalt and molybdenum, on the K_{ISCC} of NiSiCr steel in solution was studied. Addition of cobalt to NiSiCr steel resulted in an increase in K_{ISCC} whereas molybdenum addition decreased the K_{ISCC} . Combination of cobalt and molybdenum resulted in an increase in the K_{ISCC} while the combination of cobalt and molybdenum resulted in a decrease in K_{ISCC} although not as much as in the case of cobalt addition. The effect of alloying elements on K_{ISCC} could be attributed to their effect on the yield strength.

Keywords. Ultrahigh strength steels; fracture toughness; threshold stress intensity for corrosion cracking, K_{ISCC} ; segregation.

1. Introduction

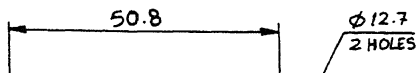
In recent years, much attention has been given to the development of ultrahigh strength steels for critical aerospace and marine applications. The properties (Garrison 1990; Tamura 1991; Garrison 1986) of these

the effect of alloying additions, viz. Co, Mo, a combination of Co and Mo, and Ce, on the K_{ISCC} of NiSiCr steel in 3.5% NaCl aqueous solution.

2. Experimental

The nominal composition in wt.% of the base NiSiCr steel was 60 Ni, 35 Si, 5 Cr. Small amounts (<1%) of Co, Mo, Ce or combination of Co and Mo were added to the base steel to study the effect of alloying additions. All specimens except NiSiCr + Co + Mo were vacuum induction melted. The base steel was produced by air induction melting followed by vacuum induction melting and had relatively higher C (0.37). Specimen blanks were solution treated and tempered at 523 K. The tensile properties and fracture toughness were determined in the longitudinal and L-T orientation, in accordance with ASTM E-8 (1991) and ASTM E-399 (1991).

Compact tension specimens (see figure 1) with $W = 50.8$ mm and $a = 25.4$ mm were used for evaluating the K_{ISCC} utilizing the double cantilever beam method. The experimental details of this technique are available in the literature (Sternberg 1976). The compact tension specimen was immersed in the corrosive solution which was constantly circulated by means of a pump. The constant stress intensity factor without crack extension was chosen for the estimation of K_{ISCC} . For all compositions, the stress intensity factor was increased by increments of $0.5 \text{ MPa}\sqrt{\text{m}}$ until crack initiation occurred. The highest stress intensity factor where crack extension was observed was considered as K_{ISCC} . The crack initiation was determined using a previously calibrated LVDT. However, the crack propagation rate (da/dN) could not be determined as the crack propagation rate is

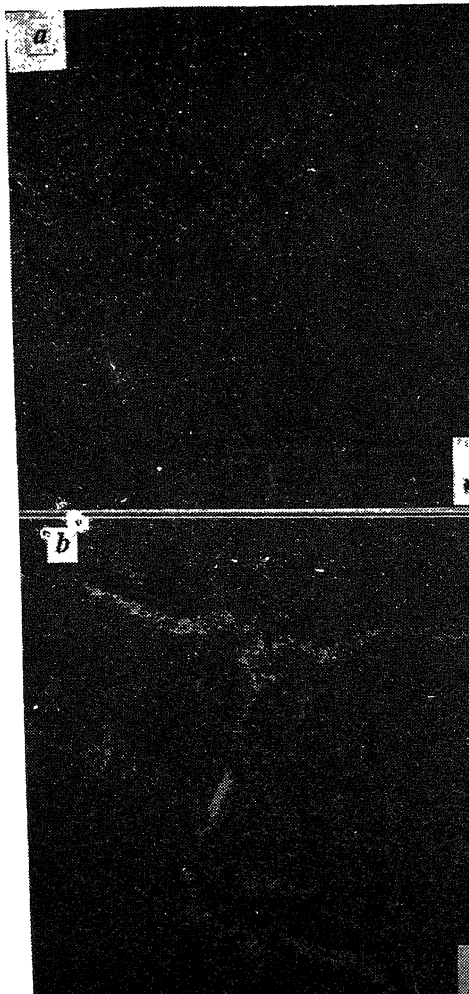


extremely rapid. A minimum of two tests were carried out. The fractured surfaces were examined in an SEM to study the mode of fracture. Probe microanalysis (EPMA) and secondary ion mass spectrometry were carried out to study the segregation of elements at the prior austenitic grain boundaries.

3. Results

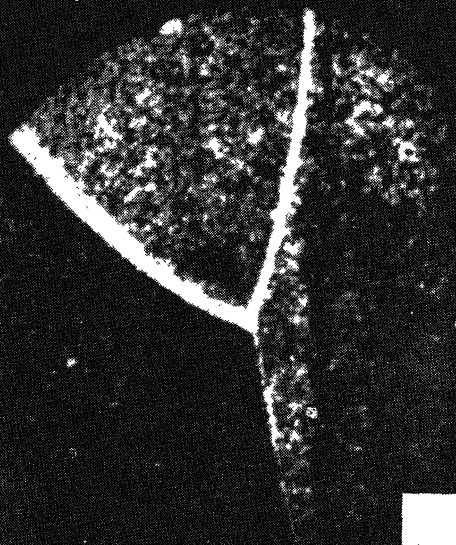
The tensile properties and fracture toughness of the steels investigated are listed in table 1. It is evident from table 1 that the addition of Co increases the yield strength and increases the fracture toughness of the base steel. The addition of Mo increases the yield strength and marginally decreases the fracture toughness of the base steel. Ce addition has no influence on either the yield strength or fracture toughness while a combination of Co and Mo results in an increase in both yield strength and fracture toughness. The K_{ISCC} values are listed in table 1. The values listed are an average of two tests with the maximum values being less than $1 \text{ MPa}\sqrt{m}$ in all cases. The trend in the K_{ISCC} values (table 1) is similar to that seen for K_{IC} with Co and Co + Mo resulting in an increase, Mo addition resulting in a decrease and Ce addition resulting in no change in the K_{ISCC} of the base steel.

Representative EPMA carbon element maps for NiSiCr steel and NiSiCr steel with Co addition are shown in figures 2a and b, respectively. Figure 2a shows that there is no preferential segregation of carbon at the prior austenitic grain boundaries in the case of NiSiCr steel while there is a significant amount of carbon at the prior austenitic grain boundaries in the case of NiSiCr + Co steel. Figures 2b and c show that NiSiCr + Mo steel exhibits a behaviour similar to that of the base steel, whereas NiSiCr + Co + Mo steel shows, again, carbon segregation at the prior austenitic grain boundaries. Representative SIMS ion images for the base steel and NiSiCr + Mo steel are shown in figures 3a and b, respectively. Figure 3a clearly reveals the segregation of carbon at the prior austenitic grain boundaries, while figure 3b shows that the addition of Mo does not lead to a significant



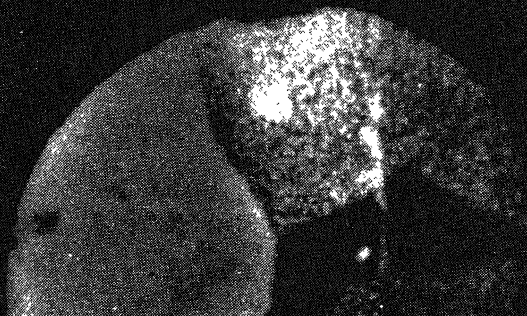
Effect of alloying additions on K_{ISCC} of NiSiCr steel

a



50 μm

b

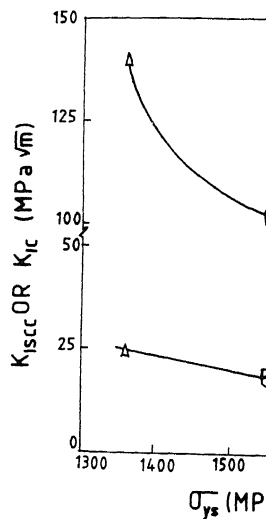
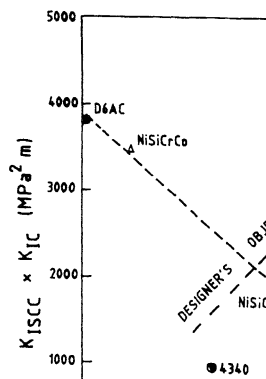




Effect of alloying additions on K_{ISCC} of NiSiCr steel

in (i) yield strength and (ii) critical fracture stress. An increase in yield strength results in an increase in the local crack tip flow stress causing the critical fracture stress to be reached at a lower applied stress intensity factor. On the other hand, an increase in the critical fracture stress, which is proportional to the strength of the grain boundary, results in a requirement of a higher applied stress intensity factor for fracture to occur.

Cobalt addition to the base NiSiCr steel results in the precipitation of carbon to the prior austenitic grain boundaries (figures 2b and 3b) which leads to an enhancement in grain boundary cohesion (Seah 1980; Messersmith 1981; Seah and Hondrous 1983; Hansen and Grabke 1986; Suzuki et al. 1990; McMahon Jr. 1991). The reason for the improvement in grain boundary cohesion with carbon segregation in iron base alloys is two-fold. Firstly, carbon displaces harmful impurities, like P (Misra and Rama Rao 1990; Tsao 1988; Misra and Rama Rao 1993), from grain boundaries. Secondly, segregation of carbon at the grain boundaries in iron base alloys promotes cohesion in the manner elucidated recently by Rice (1991). The increase in grain boundary cohesion gives rise to an increase in the critical fracture stress as is reflected in the observation of higher critical fracture stress in the fracture surface (figure 4c). The addition of cobalt results in a lowering of the yield strength. Thus, as discussed earlier, both the increase in yield strength and the increase in critical fracture stress lead to a higher K_{ISCC} in NiSiCr+Co steel. In the case of NiSiCr+Co steel, an increase in the yield strength as compared to the NiSiCr steel results in a change in the segregation of carbon atoms to the prior austenitic grain boundaries (figures 2a and 3b). Thus, the lower K_{ISCC} in this case can be attributed to the basis of the increase in yield strength because of which the local crack tip flow stress attains the critical fracture stress at a lower applied stress intensity factor (K_{ISCC}). In the case of NiSiCr+Co+Mo steel, the yield strength is higher than that of the base steel but there occurs also preferential

Figure 5. Variation of K_{ISCC} 

Effect of alloying additions on K_{ISCC} of NiSiCr steel

additions, however, results in an improvement in the K_{ISCC} of not as much as in the case of only cobalt addition.

(ii) The effect of alloying additions on K_{ISCC} of NiSiCr steel on the basis of Nair and Tien's plastic flow model for K_{ISCC} .

(iii) A superior combination of K_{ISCC} , K_{IC} and yield strength in steel alloyed with Co + Mo.

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Some new results in microalloyed steels

RAMEN DATTA
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Abstract. In recent t
the mechanisms associ
multipass hot rolling o
austenite before transfo
to the attainment of in

In the present paper, s
steel, using a hot cor
actual plate rolling or
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are also outlined.

Keywords. Thermome

1. Introduction

During a typical hot workin
subjected to hardening and
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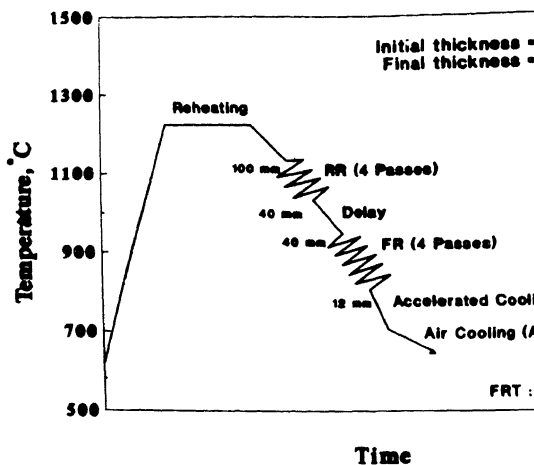


Figure 1. Schematic representation of a typical TMC investigation.

(figure 1), steel specimens were machined having a height of 10 mm (h/d ratio = 1.5). The specimens were sealed. To further minimize any oxidation effects, these quartz argon. The total pressure of each sealed tube was measured. The specimens were homogenized at 1200°C for 30 min. This treatment ensured the dissolution of nitrides and carbonitrides of titanium and boron to gamma-iron. For the austenitizing treatment, the specimens were quenched in a water-oil mixture. This treatment ensured that the composition of the specimens could be retained. The specimens were next loaded in a furnace and reheated to a temperature of 1200°C for 3 min. After the reheating treatment, the specimens were subjected to controlled deformation at various rates and temperatures followed by air cooling/water quenching. The specimen temperature during hot deformation and cooling was monitored.

Thermomechanical processing results of microalloyed steel

To simulate the hot strip rolling conditions, a series of specimens were subjected to the following TMCP schedule: (i) 1200–1000°C (33%) 20 – WQ (33%) 20 – ACRT, (iii) 1200–1000°C (33%) 20 – C (600) – ACRT (33%) 20 – 800 (50) 20 – WQ and (v) 1200–1000°C (33%) 20 – 800 (50) 20 – WQ.

To cite an example, experiment (iii) represents austenitization at 1200°C, cooling to 1000°C, deformation at 1000°C ($\dot{\epsilon} = 20 \text{ s}^{-1}$), air cooling to 600°C, coiling at 600°C for 2 h followed by air cooling to room temperature.

2.4 Tempering treatment

Here thermomechanically processed 12 mm plates (see figure 1) were subjected to tempering treatments at 550, 600 and 650°C for 1 h followed by air cooling to room temperature.

2.5 Metallography

Longitudinal sections of the hot deformed specimens and hot rolled plates were etched with 2% nital and observed under a Reichert optical microscope to distinguish between bainite and martensite, sodium metabisulfite was used as the etchant. The volume fraction of second phases was measured using a Leitz quantimet. The microhardness values of the different phases were measured using a MM6 Leitz microscope as a supplementary measure to confirm the results of metallography.

Thin foils for electron microscopy were made using a twin jet technique in a 10% perchloric-glacial acetic acid solution and studied under a JEOL 4000EX electron microscope.

2.6 Property evaluation

Tensile samples were prepared as per ASTM-10 on an Instron machine at a strain rate of 6.6×10^{-3} s⁻¹. Samples were prepared and tested at room temperature and -100°C for impact energy (IE). The temperature was 2°C .

3. Results and discussion

3.1 Hot deformation of austenite

The present investigation looked into the influence of austenite region ($\sim 1000^\circ\text{C}$) and deformation in the ferrite region ($\sim 800^\circ\text{C}$) at strain rates of 5 s^{-1} (to simulate hot strip rolling) on the austenite grain size. The steel was microalloyed with titanium and boron.

Figure 3 shows an optical micrograph of the steel after ice-water quenched, revealing packets of lath martensite. The average prior austenite grain size was estimated. To depict the microstructural changes occurring during γ -recrystallization zone. Deformation ($\epsilon = 33\%$, followed by ice water quenching (figure 4a) resulted in a fine lath martensite. A change in the cooling rate from iced-water quenching led to the formation of a typical acicular ferrite microstructure.

The microstructural changes occurring during γ -recrystallization zone was found to be similar to that of the ice-water quenching. The austenite grain size after deformation ($\epsilon = 33\%$) was estimated to be $53\text{ }\mu\text{m}$. This is similar to that observed in the γ -recrystallization zone (figure 4a). A change in cooling (from ice-water quenching to air cooling) led to a acicular ferrite microstructure.

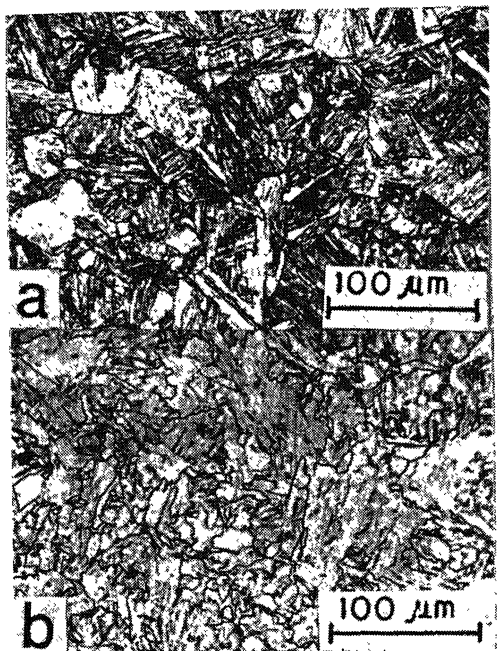
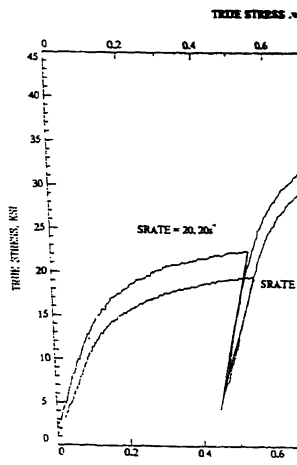


Figure 4. Microstructural changes occurring under simulated (a) $(\epsilon = 33\%, \dot{\epsilon} = 5 \text{ s}^{-1}, T = 1000^\circ\text{C})$ for a Ti-B steel followed by (b) air cooling.

It is of interest to note the nature of the flow stress curves under the simulated deformation schedule, i.e. for simulated plate ($\dot{\epsilon} = 5 \text{ s}^{-1}$) and rolling conditions. The true stress-true strain curves would show the processes of strain hardening and restoration (softening) that take place in the hit or double hit tests, with a predetermined time delay (t_d) between hits.

directed towards control rolled transformation induced plasticity (TRIP) steels (Kim and Thomas 1983; Lander *et al* 1985; Sanak Mishra *et al* 1986; Averbach *et al* 1991). Thus Kim and Thomas (1983) achieved TRIP through control rolling and quenching. Lander *et al* (1983) showed that TRIP steels have microstructures with strength and toughness comparable to linepipe steels using C-Nb and C-Nb-Ti. Averbach (1985) reported the development of TRIP in low carbon quenched Nb containing low carbon steels. On the other hand reports development of acicular ferrite in low carbon quenched Ti-microalloyed low carbon steels.

Figure 6 shows an optical micrograph of a TRIP steel exhibiting typical acicular ferrite.



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dispersed within the matrix. When the FRT was increased to 900°C , the microstructure changed from acicular to polygonal ferrite, with the presence of bainite and martensite (figure 7, FRT, 900°C). The influence of FRT on the microstructure, volume fraction of second phase and mechanical properties are shown in table 1. The volume fraction of second phase increased by 17.6% with an increase in FRT from 750 to 900°C . The average grain size was found to be insensitive to FRT, being marginally lower ($4.5\ \mu\text{m}$) at FRT of 900°C . The average microhardness values for polygonal ferrite and martensite obtained for FRT of 900°C were 165, 251 and 300 Hv_{0.05}, respectively. The acicular ferrite microstructure (FRT, 750°C) yielded the best mechanical properties (YS, 520 MPa; UTS, 660 MPa; ϵ_T , 20%; CIE (-20°C), 1.5).

Figure 8 shows a transmission electron micrograph of a plain-Ti steel finish rolled at 750°C , showing laths of acicular ferrite. A moderate dislocation density was found within the acicular ferrite ($\sim 9 \times 10^9\ \text{cm}^{-2}$). The yield strength (520 MPa) for the steel finish rolled at 750°C can be attributed to the fine grain size ($\sim 5\ \mu\text{m}$) and a moderately high dislocation density of the acicular ferrite.

Figure 9 shows a TEM micrograph of a plain-Ti steel finish rolled at 750°C , exhibiting a packet of lath martensite formed at a triple point. The higher tensile strength of this steel (UTS, 698 MPa) as compared to the ferrite steel (FRT, 750°C , UTS, 660 MPa) may be related to the formation of lath martensite and higher overall volume fraction of second phase (17.6%).

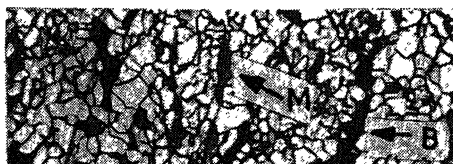
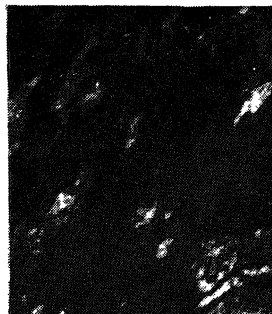




Figure 8. TEM micrograph for plain-Ti steel (FRT, 750°C)



Thermomechanical processing results of microalloyed steels

and properties of a control rolled Ti-B microalloyed HSLA steel (Rama 1991; Datta *et al* 1993).

The microstructure, ferrite grain size and volume fraction of second phase for the Ti-B steel subjected to different processing conditions are listed in Table 1. It may be noted that the austenitizing time (1 h and 3 h) does not have a significant influence on the product microstructure, ferrite grain size and volume fraction of second phase.

The cooling rate was found to have a significant influence on the microstructure and properties of the Ti-B steel. A change in cooling rate from air to water cooling led to a change in microstructure from ferrite-pearlite to ferrite-bainite. Figures 10a and b are optical micrographs of steels finish rolled at 850°C and 800°C, respectively, followed by spray water cooling. Finish rolling at 850°C resulted in a coarse bainitic structure while a lower FRT of 800°C yielded a fine ferrite-massive bainite structure. The above classification into coarse and massive bainite (Bm) structures is in accordance to that reported by Datta *et al* (1988).

Figures 11a and b represent TEM photomicrographs taken from the fine ferrite-massive bainite (800-SWC) steel. The high dislocation density within the ferrite and fine precipitates pinning the dislocations may be noted (Figure 11a). The dislocations appear mostly in tangled form. Figure 11b reveals the presence of a second phase (martensite) within a massive bainite region. Presence of a second phase (martensite/austenite) can be seen at the interface of ferrite laths in addition to fine precipitates within the laths. Similar type of substructure has been reported by Guoqing and Weixun (1985). Energy dispersive analysis of precipitates within a polygonal ferrite region of the same steel was also carried out. Analysis revealed them to be TiS type while the finer precipitates were found to be either Ti_2S or $Ti_4S_2C_2$ compounds.

Figures 12a and b show the influence of processing parameters, microstructure and tensile strength on the impact transition temperature. The transition temperature increased linearly from -72°C (800-AC, ferrite pearlite) to -35°C (850-SWC, bainite). Thus, the ferrite-pearlite steel exhibited superior toughness properties.

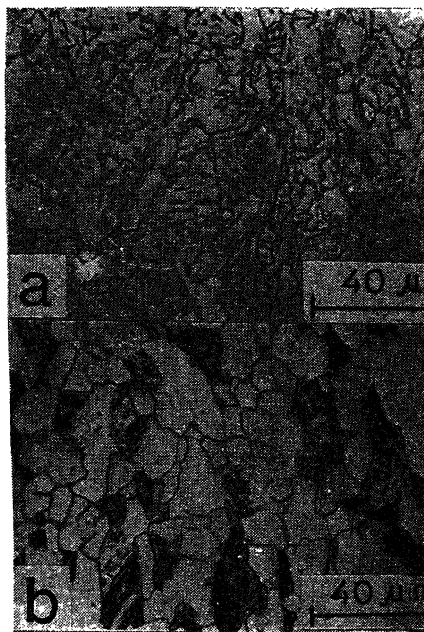


Figure 10. Optical micrographs showing typical microstructures for Ti-B steels rolled at 850 and cooled.

that of bainitic (coarse and massive) structure is significantly higher for the bainitic steels (430–460 MPa) than for the ferrite-pearlite steels (430–460 MPa).

3.4 Microstructural changes accompanying the

The present study has been carried out with the aim of

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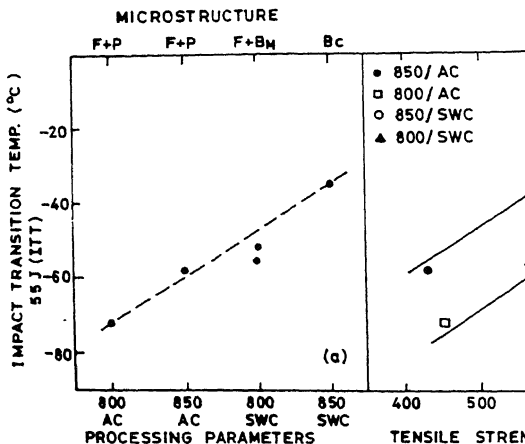


Figure 12. Influence of (a) processing parameters, microstructure on impact transition temperature for a Ti-B steel.

tempered at 650°C. Selected area diffraction studies (figure 15) show that elongated carbides are essentially cementite (Fe_3C). The decomposition of the martensite upon tempering at 600 and 650°C led to softening of the steel and concomitant improvement in impact transition temperature (USE) and ductile brittle transition temperature, as shown in the present investigation (figure 16).

Thermomechanical controlled processing led to the formation of precipitates in the as-rolled steel. These precipitates remained fine after tempering at 550°C. Figure 17a shows such precipitates within ferrite grains. The precipitates at 850°C followed by tempering at 550°C. SAD studies show that these precipitates are Nb-V (C) type ranging in size from 10 to 20 nm.

Table 3 shows the Vickers hardness values of the steel under different processing conditions. The microhardness values of the steel

Thermomechanical processing results of microalloyed ste

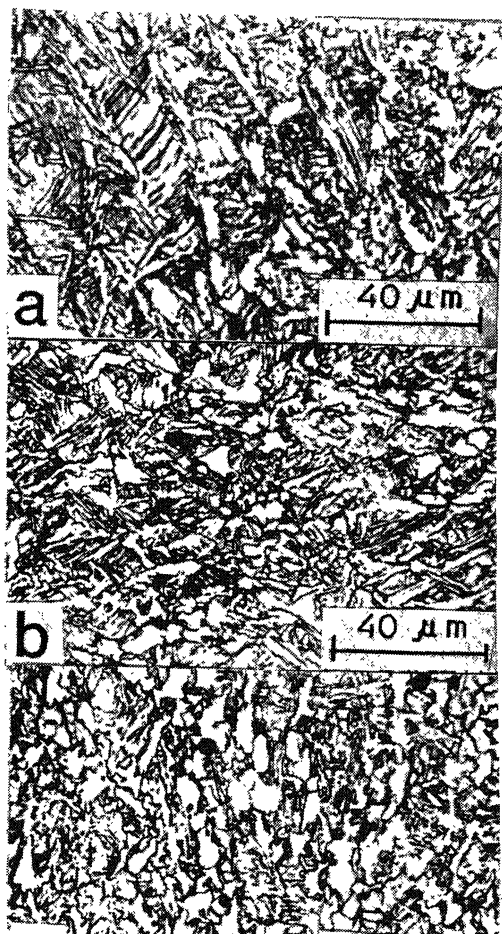
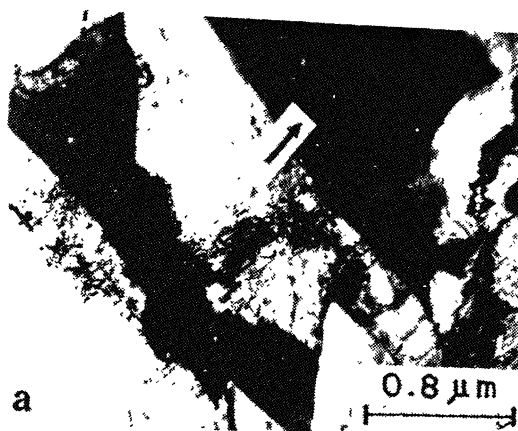


Table 3. Typical hardness, microhardness and volume for a Nb-V steel subjected to different processing conditions

Processing details			Vicker's hardness (HV)	Microhardness (HV)
FRT (°C)	Cooling rate	Tempering temp. (°C)		F
850	SWC	(As-rolled)	289	311
850	SWS	550	280	228
850	SWC	600	237	231
850	SWC	650	223	231
800	SWC	(As-rolled)	266	270
800	SWC	550	232	220
800	SWC	600	222	216
800	SWC	650	211	228



Thermomechanical processing results of microalloyed

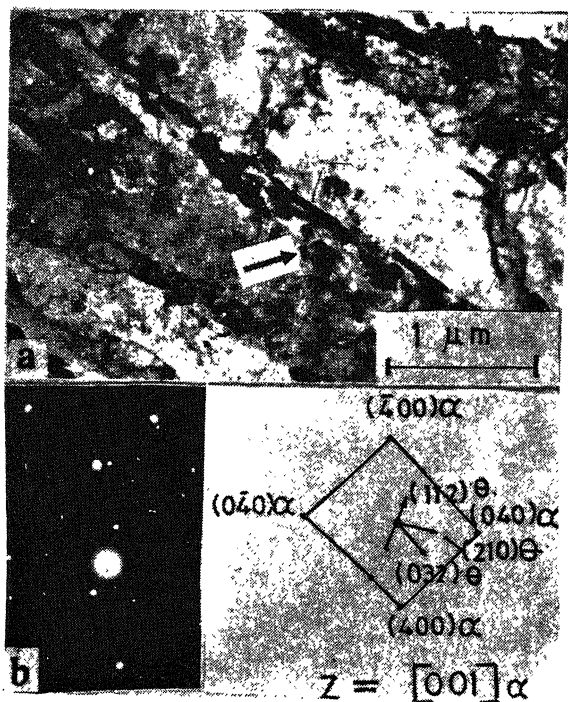
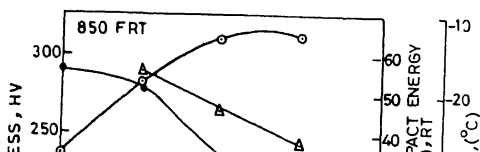


Figure 15. TEM micrograph taken from a tempered bainitic steel (0.2 mm) showing (a) precipitation of cementite (Fe_3C) within the dislocations and (b) SAD pattern from the precipitates and its interpretation.



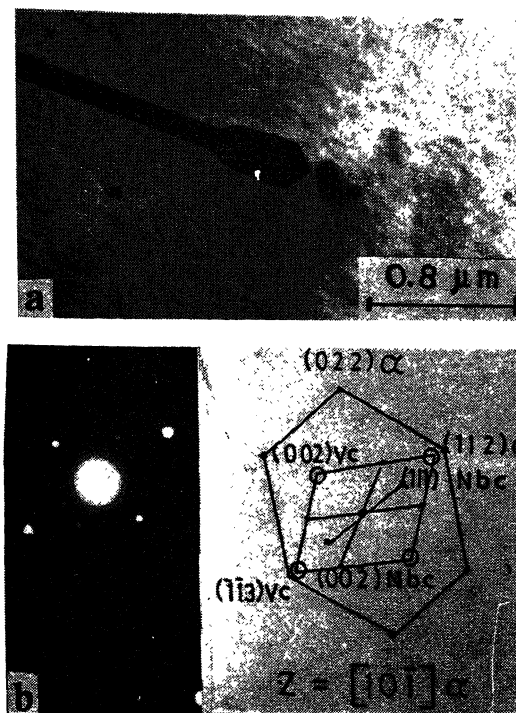


Figure 17. TEM micrograph showing (a) precipitates and (b) selected area electron diffraction pattern with interpretation for a tempered Nb-V steel.

for tempered ULCB steels. Their results showed that the hardness was insensitive to tempering treatments when tempered below 400°C. Above this temperature the hardness value decreased progressively with increasing temperature, indicating overall softening. The yield strength also showed a similar trend, with a sharp drop in yield strength above 400°C.

Thermomechanical processing results of microalloyed steel

4.2 Acicular ferrite microstructure

(i) A finish rolling temperature (FRT) of 750°C followed by spray water cooling resulted in an acicular ferrite microstructure (with fairly high dislocation density within the laths) for a plain-Ti microalloyed steel. A higher FRT of 800°C yielded a polygonal ferrite microstructure with second phase constituents of bainite and martensite.

(ii) The plain-Ti steel finish rolled at 750°C (acicular ferrite microstructure) had a good combination of properties. Typical values of strength, ductility and toughness properties obtained were: YS = 529 MPa, UTS=660 MPa, A_{50} = 22%, K_{IC} = 42 MPa $\sqrt{m}$ (–20°C)–52 J.

4.3 Bainitic microstructure

(i) Variation of austenitizing time (1200°C, 1 and 3 h) did not have a significant influence on the microstructure, grain size, volume fraction of second phase and associated mechanical properties for Ti-B steels subjected to different cooling conditions.

(ii) Finish rolling at 850 and 800°C followed by spray water cooling resulted in ferrite–coarse bainite and polygonal ferrite–massive bainite structures, respectively. The polygonal ferrite–massive bainite structure had a lower strength level but superior ductility–toughness properties compared to the ferrite–coarse bainite structure.

4.4 Microstructural changes accompanying tempering

(i) Finish rolling at 850°C followed by SWC led to a microstructure consisting of ferrite and bainite. Tempering at 400°C for 1 h resulted in a microstructure consisting of ferrite and bainite. Tempering at 500°C for 1 h resulted in a microstructure consisting of ferrite and bainite. Tempering at 600°C for 1 h resulted in a microstructure consisting of ferrite and bainite. Tempering at 700°C for 1 h resulted in a microstructure consisting of ferrite and bainite. Tempering at 800°C for 1 h resulted in a microstructure consisting of ferrite and bainite. Tempering at 900°C for 1 h resulted in a microstructure consisting of ferrite and bainite. Tempering at 1000°C for 1 h resulted in a microstructure consisting of ferrite and bainite.

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Creep strain prediction of 2 ¼ Cr 1Mo A model based approach

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Abstract. The paper examines the potential of a model creep behaviour of 2 ¼ Cr 1Mo steel. Effects of prior str shape of the creep curve have been experimentally establishe identified as the dominant mechanism of creep. Creep curve particle coarsening model have been compared with those o microstructural conditions.

Keywords. Deformation mechanism; strain softening; parti tertiary creep; damage mechanism.

1. Introduction

2 ¼ Cr 1Mo steel is extensively used in high temperature because of its excellent creep resistance. Although simple test data on such steel over a range of stresses and temperatures to satisfy the current needs of the designer, with growing design technique, there is now considerable interest in characterizing the complete creep strain time plots of such materials. Unlike phase alloys they rarely exhibit a well established steady state after a small primary strain the creep rate progressively increases in value ($\dot{\epsilon}_i$) until fracture. The level of sophistication of analytical element method depends on the ability to accurately represent the creep rate and deformation mechanism and temperature. Recently

Clearly a set of 16 constants are required to characterize an engineering material. The main problem of this approach is extrapolation beyond the domain of available test data and a large volume of test data to obtain 16 material constants.

The mechanism based approach however does not suffer from this. The one developed by the high temperature materials group at the Laboratory, Teddington and Cambridge University deserves mention (Dyson and Dyson 1984; Barbosa *et al* 1988). Dyson and McLean (1983) reviewed the current status of this approach. Based on the experimental curves more emphasis has been placed on the contribution of different damages. Following Ashby and Dyson (1984), damages responsible for creep are classified into three categories: (i) Microstructural changes (e.g. precipitate size etc.) that reduce the strength of material, (ii) change in grain section size due to geometrical changes that leads to a change in the loading condition (ω_2) and (iii) loss of internal load bearing capacity due to cracking which commonly occurs at grain boundaries (ω_3).

The damage parameter ω_i ($i = 1, 2, 3$) can be defined in terms of forms of equations relating creep strain and damages having been developed on the basis of the current understanding of deformation mechanisms. For example materials exhibiting strain softening the creep law has been represented as:

$$\dot{\epsilon} = \dot{\epsilon}_i \exp (\omega_1 + \omega_2 + \omega_3),$$

$$\dot{\omega}_1 = C_1 \dot{\epsilon},$$

$$\dot{\omega}_2 = C_2 \dot{\epsilon},$$

$$\dot{\omega}_3 = C_3 \dot{\epsilon},$$

where $\dot{\epsilon}_i$, C_1 , C_2 , C_3 are the model parameters for a given material (Barbosa *et al* 1988; Dyson 1988; Dyson and Gibbons 1988; and McLean (1983), appropriate model for materials exhibiting strain softening).

Creep strain prediction of 2 1/4 Cr 1Mo steel

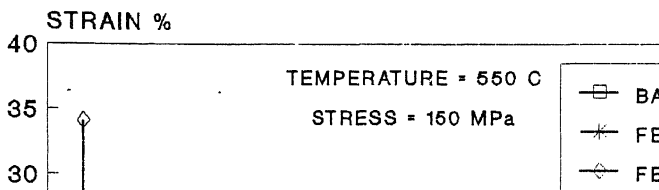
stress creep data where the effect of decreasing cross section by proportionate load reduction it is not necessary to consider ω_2 . Consequently the tertiary creep behaviour of single crystal strain softening could be considered by a set of two equations (al 1990):

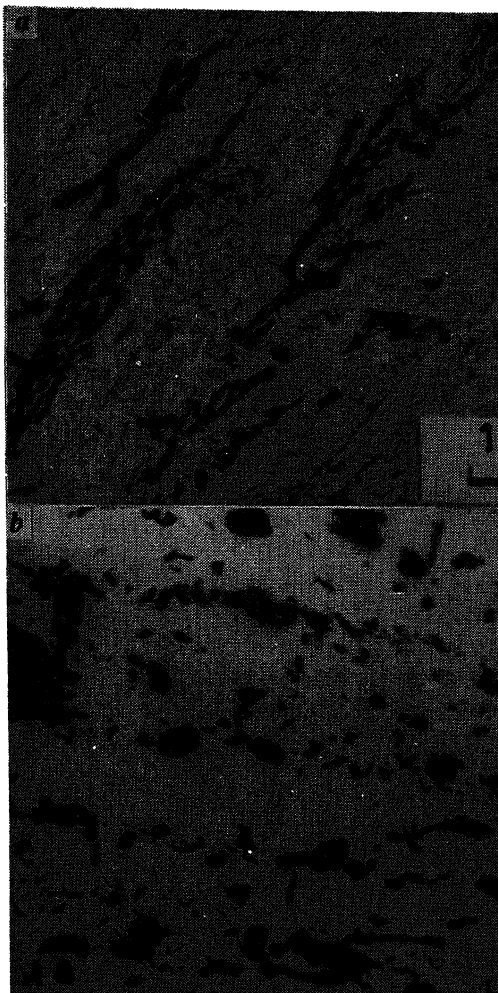
$$\begin{aligned}\dot{\epsilon} &= \dot{\epsilon}_i \exp(\omega_1), \\ \dot{\omega}_1 &= C_1 \dot{\epsilon}.\end{aligned}$$

The present work examines the creep behaviour of 2 1/4Cr 1Mo steel the dominant mechanism of deformation so that a simple model for creep strain prediction could be developed.

2. Mechanism of creep deformation

Creep strain-time plots of 2 1/4Cr 1Mo steel given in figure 1 show microstructural conditions clearly reveal the dominant influence. Typical microstructures of this steel before and after creep exposure 2 show significant coarsening of carbide. Softening due to grain boundary sliding therefore appear to be the obvious mechanism for the continuing creep rate. However in the case of superalloys in spite of particle coarsening evident from microstructural examinations, strain softening of dislocation density was identified as the dominant mechanism.





Creep strain prediction of 2 1/4 Cr 1Mo steel

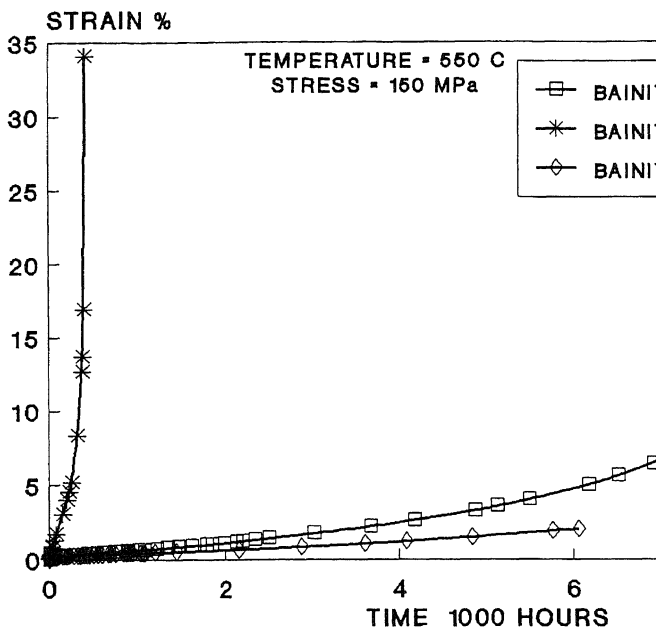


Figure 3. Effect of thermal aging and prior cold work on creep strain of 2 1/4 Cr 1Mo steel at 550°C, 150 MPa.

can be neglected (i.e. $\omega_3 = 0$). Assuming that the minimum power law kind of stress dependence with n as the stress exponent, the change in cross sectional size under constant load creep can be expressed as (Dyson 1964):

It has been shown that under such cases $C_2 = n$ (Dyson 1964). The load creep strain time plots of 2 1/4Cr 1Mo steel could be expressed as:

$$\begin{aligned}\dot{\epsilon} &= \dot{\epsilon}_i (1 + \omega)^n \exp(n\epsilon), \\ \dot{\omega} &= a (1 - b\omega)^4,\end{aligned}$$

with an experimental creep curve reported by Maruyama *et al*. The curves used to estimate the material constants even though the grade of steel were from a totally different source (Wolf). In spite of this fact the matching between the experimental and the predicted curves is excellent. Since these steels are susceptible to time softening with long exposure, the difference in the shape of predicted and experimental curves will depend on whether the initial microstructures were similar. The creep tests were carried out in our laboratory on 2 1/4Cr 1Mo steel with different initial microstructures, viz. 100% bainite, ferrite + bainite and ferrite + pearlite. Figures 1 and 5 show the influence of initial microstructure on the creep behavior.

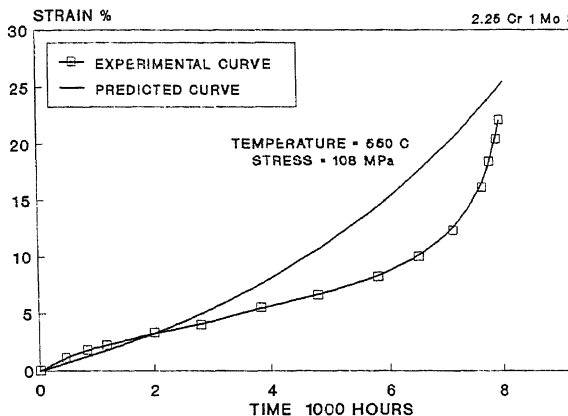
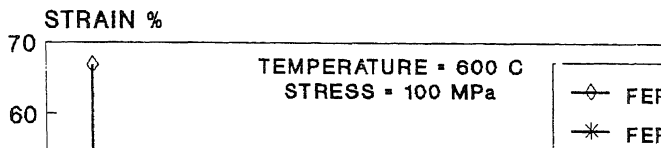


Figure 4. Comparison of theoretically predicted creep curve and experimental data reported by Maruyama *et al* (1990).



Creep strain prediction of 2 1/4 Cr 1Mo steel

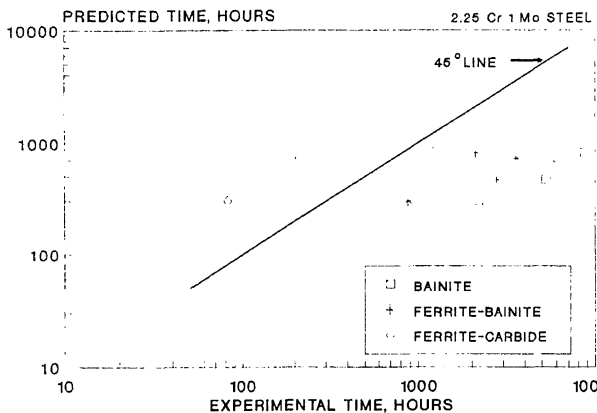


Figure 6. Comparison of predicted and experimental time to failure for different microstructural conditions.

time plots. Clearly the structure having ferrite and globular carbide has the best creep resistance. Theoretically calculated creep curve using the data from an analysis of creep curves used by Wolf (1990) has also been shown on figure 5. The fact that this does not match with any of the results obtained in this work is not surprising. This is primarily because the microstructure (particle size) in these cases is different. The comparison of the calculated and predicted time to reach a creep strain of 5%. This shows predictions in general are closer to experimental results for carbide structure indicating that the microstructures of the data from Wolf (1990) and Maruyama (1990) consisted of ferrite and carbide. The results presented indicate that there is a need to generate a database of data on Cr Mo steel in terms of its initial microstructure. This work is currently in progress in our laboratory.

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Metallurgical aspects of corrosion

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Abstract. Metallurgical properties have strong effects on corrosion and reviews the work done at CECRI on the metallurgical aspects of industrially important alloys like steel and aluminium alloy weldments, steel and prestressing steel. The corrosion control methods for these alloys are reviewed.

Keywords. Weldments; corrosion; maraging steel; heat treatment; peening.

1. Introduction

Metallurgical properties have strong effects on corrosion. The corrosion resistance of materials is increased by addition of alloying elements, heat treatment techniques. A major constraint for these techniques is increased susceptibility to stress corrosion cracking above certain strength levels. Many failures have occurred due to stress–environment interaction. The relation between stress, mechanical properties, environment and corrosion resistance is critical to the proper application of many materials in various sectors. Many of the mechanical properties and the corrosion resistance can be related to its heat treatment. Welding affects the mechanical properties and corrosion of the weldment. Metallurgical aspects of stress corrosion are carried out at the Central Electrochemical Research Institute, Karaikudi and this paper discusses and reviews the following metallurgical aspects: (i) corrosion of steel and aluminium alloy weldments (ii) corrosion of

the weld metal is cathodic with respect to the base metal. This is less serious because the attack is distributed over the weld metal. There have been reports of corrosion rates of up to 0.1 mm/year (ASTM 1961). This severe corrosion was attributed to the potential difference between the weld metal and the base metal. The potential difference is a more strongly electronegative behaviour of the weld metal. The weld metal is primarily responsible for the potential difference between the weld metal and the base metal. The weld metal is responsible for the processes and heat treatment.

Preferential weld metal corrosion has been observed in welded structures, ASTM A36 steel was joined by shielded metal arc welding (SMAW). Cathodic protection is not used. Pitting corrosion pits are seen only on the weld metal. We have observed pitting corrosion, galvanic corrosion, cathodic protection. Tuticorin seawater to know the reasons for pitting corrosion. To prevent pitting corrosion on the welds (ASTM 1961).

2.1 *Materials and welding*

The chemical composition of the ASTM A36 steel is given in table 1. A36 steel was joined by shielded metal arc welding using E 7018 supertherme weld electrode. The weld metal thickness is 3.15 mm to 4 mm. The welding parameters are given in table 1. The heat treatment for the weld metal specimens is 600°C for 1 h after which the specimens are cooled.

Table 1. Chemical composition of the weld metal and base metal.

Steel	C	Mn	S	P
A 36	0.15	1.17	0.018	0.013
API 2H	0.23	1.17	0.010	0.011
Weld metal	0.07	1.03	0.021	0.010

Metallurgical aspects of corrosion

2.2 General corrosion

2.2a Polarization studies: The general corrosion behaviour in 3.5% NaCl solution and synthetic seawater was determined from polarization curve studies and the results are given in tables 3 and 4 respectively. From the tables that the corrosion rate of the weld metal is higher than the parent metals. Postweld heat treatment improves the corrosion resistance. As seen from table 4 that the corrosion rates in synthetic seawater for A36 steel and A36 weld metal are $8.4 \mu\text{A}/\text{cm}^2$ and $9 \mu\text{A}/\text{cm}^2$, respectively while for the weld metal the corrosion rate is $15 \mu\text{A}/\text{cm}^2$. Thus, the weld corrodes faster than the parent metals. After post-weld heat treatment, the corrosion rate of the weld metal is $7 \mu\text{A}/\text{cm}^2$ which is equivalent to the corrosion rate of the parent metals.

2.2b Electrochemical impedance measurements: Impedance measurements were carried out on the weld metal, parent metals and PWHT metal at the corrosion potential in the frequency range of 10 kHz to 0.1 Hz using Model M 378 impedance measurement system, EG and G. Figure 5 shows the impedance diagrams for the weld metal, PWHT metal and parent metals. The charge transfer resistance values, estimated from the diagrams, are given in table 5. The charge transfer resistance is inversely proportional to the corrosion rate. The weld metal has low R_t value than the parent metals, indicating higher corrosion rates than the parent metals. Post-weld heat treatment significantly improves the corrosion resistance.

2.3 Pitting corrosion

The resistance of the weldments to pitting corrosion was determined in 10% NaOH + 600 ppm chloride and synthetic seawater + 10^{-5} M Na_2S .

Table 3. Polarization data in 3.5% NaCl solution.

Corrosion current

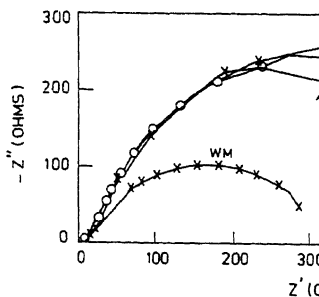


Figure 1. Impedance diagram in

Table 5. The charge transfer resistance values estimated from the impedance measurements.

Metal	Charge transfer resistance value (Rt. cm ²)
API 2H steel	487
A36 steel	667
Weld metal	300
PWHT metal	645

polarization studies. The pitting potentials in these solutions are given in tables 1 and 2. The corrosion resistance of the weld metal is lower than the parent metal resistance of weld metal.

2.4 Galvanic corrosion

Metallurgical aspects of corrosion

which make it more nobler than the weld metal. Hence, the steel has higher galvanic current density than the weld—A36 couple.

The galvanic currents measured for the weld coupled to A36 steel are for an area ratio of 1 : 1. But, in the existing structure the area ratio between the weld metal and parent metals is very much higher and hence higher galvanic currents may be expected between the weld and parent metal couples.

Weld metal corrosion in ships was attributed to the galvanic corrosion between the weld metal and parent metal (Uusitalo 1966). Premature failure of steel pipe by weld corrosion in the process stream was observed. This was due to the galvanic corrosion between E 6010 weld metal and steel pipe and weld was anodic with respect to the steel pipe.

Table 6. Pitting corrosion data in 0.04 N NaOH + 600 ppm chloride.

Metal	Pitting potential (mV vs SCE)
API 2H steel	+ 245
A36 steel	+ 110
Weld metal	+ 95

Table 7. Pitting corrosion data in synthetic sea water + 10^{-5} M Na₂S.

Metal	Pitting potential (mV vs SCE)
API 2H steel	- 814
A36 steel	- 773
Weld metal	- 848
PWHT	- 805

PWHT improves the galvanic corrosion resistance of API 2H steel couples. The weld corrosion can be eliminated by using a balanced electrode material.

Matching composition electrodes are preferred for the welding of API 2H steel. If unalloyed weld electrodes are used, the weld itself acts as an anode (Uusitalo 1966). Alloying elements are added to the electrode to achieve a balance of modifying or controlling the chemistry of the weld metal. Welds with increased copper or nickel were more resistant to localised corrosion (Nelson 1989). 1.1% Cu and 0.72% Ni were added to the E70T-1 electrode. The galvanic corrosion resistance was improved. In welding of API 2H steel vs A36 couple, weld is cathodic. In general, it would be expected for the weld metal to be somewhat cathodic because of its relatively higher nobility with parent metal.

2.5 Field exposure studies

Weldments of size 6' x 4' with the weld at the centre were exposed for 3 m inside the sea at Offshore Platform and Marine Laboratory (located at CECRI, Karaikudi). Figure 2 shows the surface appearance of the weldment after 1 month of exposure. Corrosion occurs first on the weld metal, which is not attached to the weld samples during this test period. After 1 month, attachment of barnacles are observed on the welded surface. The number of barnacles attached on the weld zone and the parent metal was counted. Since the weld metal is rough, a large number of barnacles were attached to the weld zone as compared to the parent metals. After 3 months, the specimens showed preferential weld zone corrosion (Figure 3).

2.6 Cathodic protection

The most common method of preventing corrosion of steel in seawater is cathodic protection. Pitting corrosion >5 mm in depth was observed on the weld zone.

Metallurgical aspects of corrosion

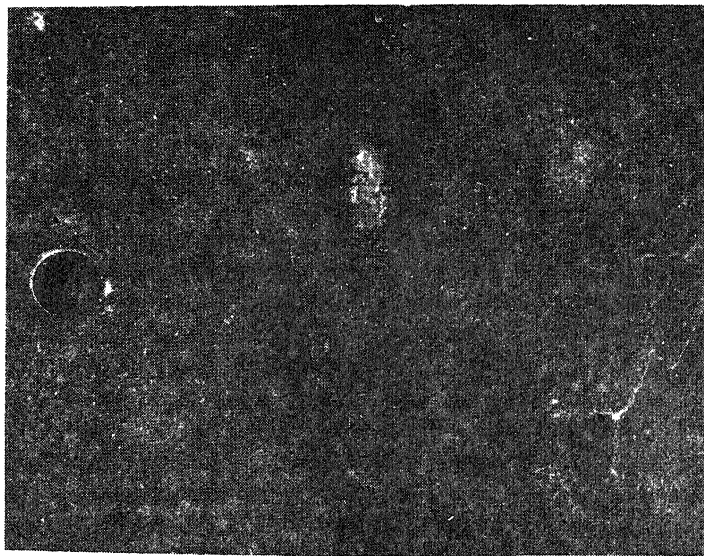
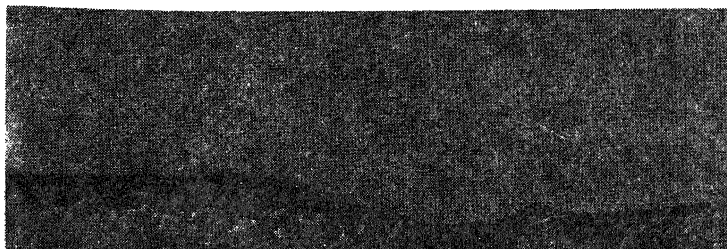


Figure 2. Corrosion products on the weld zone after one month in seawater.



on SMA and PWHT welds for 120 h. To compare the results of impedance measurements, the corrosion rate for weld metal is minimal. For PWHT it is minimal at -900 mV. The results correlate well with results from the literature.

Pitting corrosion has been observed on node welds at -850 mV vs Ag/AgCl (Du Yu *et al.* 1989). Many intersecting structural members are present at high density. Hence, these node welds are susceptible (Toncre 1980). The pit observed on the node welds under cathodic protection is attributed to the presence of welds. Now the platform is adequately protected. As reported to the US Department of Transportation, it showed that 76% of the external corrosion was due to weld corrosion. Potentials more negative than -850 mV vs Ag/AgCl are necessary to prevent pits (Toncre 1989). Polarized potentials more negative vs Ag/AgCl are necessary to protect the welds. Prevention is desired (Gummow 1989). The sample reveal that protection potential of -900 mV vs Ag/AgCl is required to protect the welds.

3. Corrosion of 7020 aluminium

Aluminium alloy is used for aerospace tanks. The general and stress corrosion cracking of 7020 sheet in T6 temper welded using (Gummow 1989).

Table 9. Average number of pits per cm² attached to the weld metal and parent metals.

Material	Average number of pits per cm ²
Weld metal	1.5
Parent metal	0.5

Metallurgical aspects of corrosion

metal and (iii) AG 5 filler metal were determined in liquid N_2O_4 . The filler metal for fabrication of tanks to handle N_2O_4 (Balakrishna et al., 2004)

3.1 General corrosion

The general corrosion resistance of these weldments was evaluated in electrochemical studies for 30 days and electrochemical impedance measurements. The corrosion rates after 30 days of immersion in liquid N_2O_4 are given in Table 3.1. It shows that 7020 welded with AG4Z2 has higher general corrosion rate compared to other filler metals. The corrosion rate of this AG4Z2 weld is 4 times higher than the parent metal. The corrosion rate of other filler metal AG 4 is 2 times higher than the parent metal, and another AG 5 filler metal is 3 times more than the parent metal.

The electrochemical impedance measurements were carried out on the parent metal as well as on the welded sheets in N_2O_4 liquid using the electrochemical analyzer (Model 1174, Solotron, UK) and the electrochemical impedance spectroscopy (EIS) (Model 1174, Solotron) over a frequency range of 1 Hz to 10 kHz. The results are given in figure 4. The alloy welded with AG5 filler metal shows a higher corrosion rate from that of other samples. The depressed semi circle of AG 5 indicates the presence of a charge transfer reaction mostly corresponding to the dissolution of the alloy. In the case of parent metal and other two filler metals, the diffusion control behaviour occurs due to the presence of passivating oxide layer.

3.2 Stress corrosion

The stress corrosion behaviour of the parent metal and the welded sheets was evaluated in liquid N_2O_4 by short term and long term SCC tests.

3.2a Short term SCC tests: Constant load tests were used. The tests were carried out by means of spring loaded test set-up. Stress applied was 18.1 MPa.

samples were exposed to liquid N_2O_4 for 6 h. The parent metal specimens were examined using optical microscope after 6 h of exposure. No cracks were observed near the weld line-plate joint with AG4.5Mn and AG4Z2 filler metal. No cracks were observed in AG4Z2 filler metal and parent metal. The short term SCC tests show that the welded sheet with AG4Z2 is resistant to SCC in liquid N_2O_4 at the stress level of 18.1 kg/mm².

3.2b Long term SCC test: Bent beam technique (four-point) was used to apply stress. 8.2 kg/mm² stress was applied to the parent metal specimens and then they were exposed to liquid N_2O_4 for 100 days. The specimens were examined using optical microscope after 100 days of exposure. Corrosion cracks were seen on the welded specimens with the same stress level as the parent metal during this period of testing. The general corrosion studies in liquid N_2O_4 reveal that alloy welded with AG4Z2 filler metal has better resistance than the other AG4.5 Mn and AG5 filler metals.

4. Effect of heat treatment on corrosion of stainless maraging steel

4.1 Stainless maraging steel

The corrosion behaviour of the stainless maraging steel depends on the composition and heat treatment. The general corrosion resistance is maximum in solution heat treated condition. Aging, depending on the temperature, affects the corrosion resistance of stainless maraging steel considerably. Lower temperature has better corrosion resistance than the higher temperature.

The stress corrosion cracking resistance varies with aging temperature. Marine environments which produce SCC in other high strength steels do not produce cracking in stainless maraging steels. Overaging improves the SCC resistance (McDarmaid 1982). Coatings or cathodic protection can be used to protect the stainless maraging steel in marine environments.

Metallurgical aspects of corrosion

overaged conditions were determined in 3.5% NaCl solution and impedance measurements. The results of the studies are given in table 14. It can be seen from the table that overaged sample has higher corrosion resistance than the underaged sample.

4.4 Pitting corrosion

The pitting corrosion resistance of underaged, peakaged and overaged maraging steel was evaluated in 0.04 N NaOH containing 10% NaCl by potentiodynamic polarization studies. The pitting corrosion current densities are given in table 14. The overaged sample has higher pitting corrosion resistance than the underaged and peakaged samples. Electropolishing in $\text{H}_3\text{PO}_4 + \text{H}_2\text{SO}_4 + \text{C}$ improved the corrosion resistance.

4.5 Stress corrosion

Stress corrosion tests were carried out on underaged and overaged maraging steel in 3.5% NaCl solution. The stress applied was 80% of proof stress. The results of the studies are given in table 15. It can be seen from the table that overaged sample has higher stress corrosion resistance than the underaged sample.

Table 11. Chemical composition of stainless maraging steel.

	Cr	Co	Ni	Mo	Ti	Al
Element%	12	12	4	4	0.5	0.3

Table 12. Mechanical properties.

	0.2% Yield strength	Ultimate tensile strength	Elongation	Hardness
Heat				

Table 14. Pitting corrosion behaviour in 100 ppm chloride.

Type of heat treatment	Heat treatment conditions
Mechanical polishing	
Underaged	450°C
Overaged	450°C
Electropolishing	
Underaged	450°C
Peakaged	450°C
Overaged	450°C

Table 15. Constant load SCC test results.

Aging	Time to failure (h)
Underaged (450°C/4 h)	100
Overaged (450°C/7 h)	300

Stress: 80% of proof stress; medium

significantly improves the stress corrosion resistance. At a stress level thirty times higher stress corrosion resistance is obtained.

5. Effect of shot peening on stress corrosion resistance

Prestressing steels are vulnerable to stress corrosion cracking when held under permanent tension while in contact with moisture. In concrete bridges, tanks and ground anchors, prestressing wires (Corbett, 1964; Szlendak, 1966)

Metallurgical aspects of corrosion

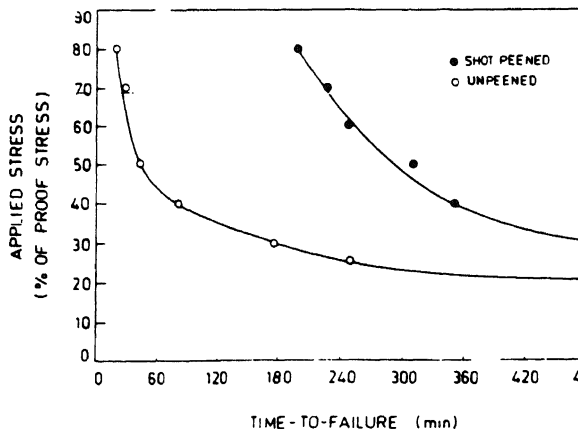


Figure 5. Applied stress vs time-to-failure data in 20% ammonia solution at 500 mV cathodic.

surface compressive stresses, and removes notches and is responsible for stress considerations by producing small shall (Metals Handbook 1982). The surface compressive stress in helps to lower the level of applied tensile stress at the superimposition of internal stresses and external applied 1 peening mainly helps to delay the initiation of the stress cor

6. Conclusions

Welding affects the metallurgical properties of the weldment. corrosion rate of the weld metal. Higher cathodic protection to prevent corrosion of weld metal. Post weld heat treatment the corrosion resistance of weld metal Weld electrode conta

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On the stress corrosion cracking mechanism in austenitic stainless steels

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Abstract. In this paper, experimental results on stress corrosion cracking in austenitic stainless steels are described. Crack growth data in sodium chloride solution and austenitic steel obtained for different metallurgical conditions, acoustic emission data on crack growth and fractographic observations have been discussed to understand the operating mechanism. Some of the experimental observations include: (i) occurring in discontinuous jumps of the order of a few microns; (ii) dependence of stress intensity and J -integral values on sensitization and cold work; (iii) fractographic features, transition in mode of fracture from transgranular to intergranular; (iv) sensitized conditions and activation energies of the order of 50 kJ/mol are accounted by hydrogen embrittlement mechanism. Hydrogen generated during the corrosion reaction diffuses ahead of the crack tip under hydrostatic pressure during the deformation process at the crack tip and also leads to the crack advance in jumps.

Keywords. Austenitic stainless steel; stress corrosion cracking mechanism; acoustic emission; fractography; hydrogen embrittlement; transgranular and intergranular fracture.

1. Introduction

There are many similarities between stress corrosion cracking (SCC), hydrogen embrittlement (HE) and liquid metal embrittlement (LME). Many suggested mechanisms seem to give a satisfactory explanation for the phenomena found in these embrittlement phenomena. Different processes are observed under specific sets of metallurgical and environmental conditions.

2.1 *The slip dissolution model*

The unit process in the slip dissolution model (Jones 1973) is the breaking of the passive film at the crack tip. The local transient dissolution of the metal at the crack tip of crack corresponds to a series of t

2.2 *A unified mechanism of SCC and HE*

In this model proposed by Jones (1985), the mechanism of crack growth; vacancies formed at the crack tip which migrate to critical lattice sites and during corrosion fatigue cracking, the vacancy sources from cyclic deformation.

2.3 *Hydrogen embrittlement (HE) mechanism*

The phenomenon of stress corrosion cracking has many similarities: in particular, both the crack initiation, discontinuous crack propagation and reaction at the crack tip is a source of hydrogen by providing the brittle component.

2.4 *Surface mobility mechanism*

A mechanism based on surface mobility (Jones 1990). The mechanism has been developed by Jones (1990) of surface vacancies to or emission of surface vacancies to Rhead (1975), high surface mobility on the metal surface. Although the mechanism is not supported for many experimental observations.

In view of the ambiguity in the various mechanisms for stress corrosion cracking in austenitic stainless steels, an attempt has been made to identify the dominant mechanism by combining fracture mechanics, acoustic emission, and fractographic approaches in the present study.

3. Experimental

The material chosen for the investigation was a nuclear grade austenitic stainless steel type 304 with a chemical composition of C 0.04%, Cr 18.3%, Mn 0.03%, Si 0.37%, S 0.003%, P 0.023%, N 860 ppm, and balance Fe. The material was available in the form of plates of the size $5000 \times 2000 \times 10$ mm in the mill-annealed condition. The different treatments given to the mill-annealed material are listed in table 1. Cold work was given by multipass rolling at room temperature.

The stress corrosion test samples were sub-size compact tension (CT) samples with a width of 30 mm and thickness of 10 mm conforming to ASTM A381-80. The specimens were machined such that the notch was perpendicular to the rolling direction. CT samples were precracked using a precracker (Model 1000, Materials Test Systems, USA) at stress intensity factor K_I values ranging from 10 to 18 MPa.m^{1/2}. The crack was grown to a length of 10 mm in the range of 25 to 18 MPa.m^{1/2}. The crack was grown to a length of 10 mm.

For crack growth studies, an acidified sodium chloride solution was used. The solution was 5 M NaCl + 0.15 M Na₂SO₄ + 3 ml/l of HCl was used. The tests were conducted at room temperature (300 K). The tests were conducted with a constant load condition (381 K). To facilitate evaluation of activation energy for crack growth process, tests at two other temperatures (363 K and 373 K) were also carried out. Both increasing K_I (constant load) and decreasing K_I (wedge loading) tests were carried out. The average crack growth rates were determined from the change in crack lengths on fracture surfaces using nine-point average method. K_I tests were used to generate data for crack growth rates. Crack growth rates of less than 1×10^{-10} ms⁻¹ were generated from the CT samples.

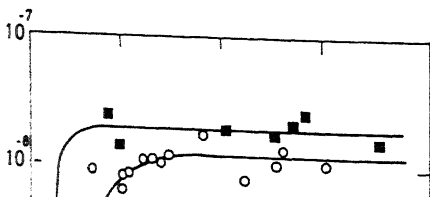
4. Results

4.1 Crack growth data

The results obtained on solution annealed and sensitized materials the parameters K_I and J_I respectively in figures 1 and 2. The shapes look similar; there is a threshold K_I or J_I (the threshold values were determined from wedge loaded, constant displacement tests); above the respective threshold a large increase in crack growth rates takes place and then reaches a plateau. Sensitization reduced the threshold values and increased the plateau crack growth rates. The shapes of the curves for other metallurgical conditions are similar. The crack growth data for all the metallurgical conditions are summarized in figure 2. The threshold values were found to be lower for the cold worked material than those for sensitized and solution annealed conditions. The threshold values, however, were also lower (in the cold worked condition). Sensitization, however, were also lower (in the cold worked condition). Sensitized material showed slightly improved threshold values but lower crack growth rates in the plateau. Influence of cold work is overshadowed by that of sensitization. The maximum crack growth rate in 20% cold worked material was found to be the same as that for solution annealed material. The threshold value was lower.

4.2 Results of activation energy measurements

Figure 3 shows Arrhenius plots of crack growth rate vs $1/T$ for



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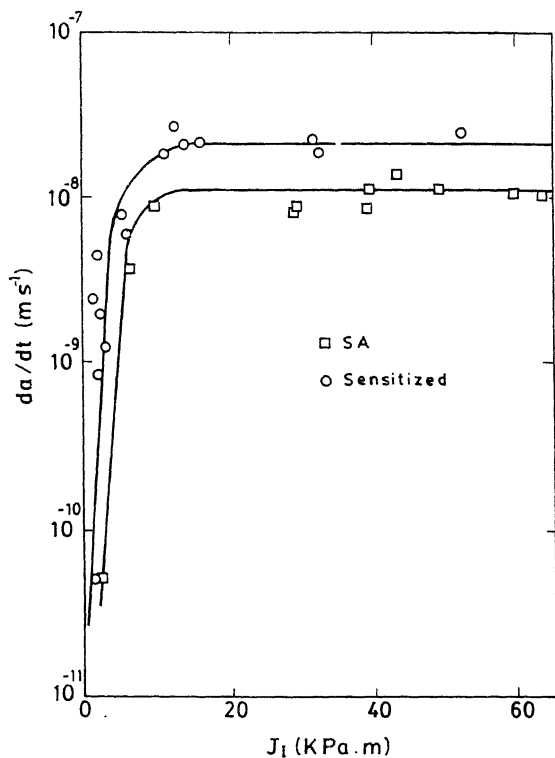


Figure 2. Influence of sensitization on crack growth rate of AISI 304 stainless steel as a function of J -integral in 5 M + 0.15 M Na_2SO_4 + 3ml/l HCl at 381 K.

Table 2. Summary of crack growth data.

4.3 Results of acoustic emission

Acoustic events were measured for solution annealed materials. The number of acoustic events per unit time in all the cases. A typical record of acoustic signal for a solution annealed material is

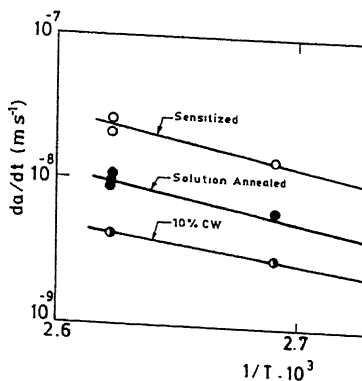


Figure 3. Variation of crack growth rate with temperature for solution annealed, sensitized and 10% CW materials in 3ml/l HCl.

Background noise (No load)

and crack growth per event computed from acoustic emission data are presented in table 3. The crack growth per event was 15 µm for a solution annealed material to 15 µm for 10% cold worked material.

4.4 *Fractographic observations*

4.4a Solution annealed material: Mode of fracture was found to be transgranular irrespective of stress levels. A typical fan-shaped pattern was observed at initiation. Crystallographic pits, secondary cracks on river lines were also seen. Figure 5a shows river lines and fan-shaped pattern. A number of parallel lines/cracks perpendicular to river lines were also seen (figure 5b).

4.4b Cold worked material: The fractographic features observed on cold worked materials were similar to those seen on fracture of solution annealed material. Density of fan-shaped pattern was found to be higher in cold worked condition. Fans were not clearly delineated at the end of crack.

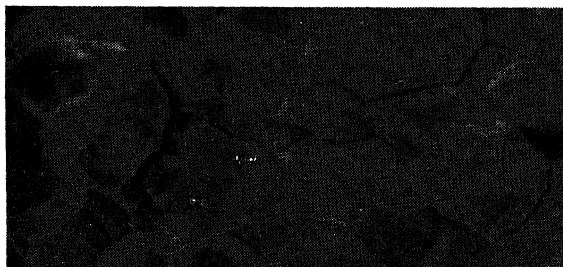
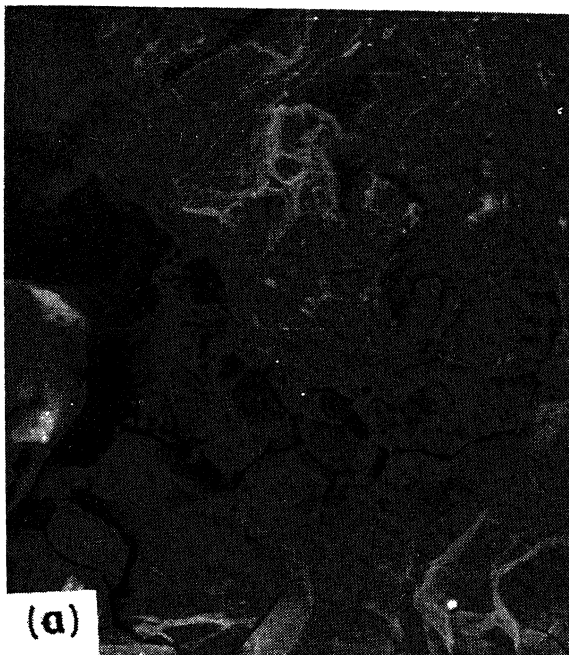
4.4c Solution annealed + sensitized material: The crack in solution annealed + sensitized material was transgranular mode irrespective of test method and stress levels. Fracture along the edges was transgranular. However, there was a transition from transgranular to intergranular in the mid thickness region. Fracture at different stages of crack propagation along the central line was transgranular. Transition from transgranular to intergranular is seen in figure 6a. In figure 6b fully intergranular fracture is seen. The transgranular fracture was observed in the edge region.

Table 3. Acoustic emission data obtained during crack growth.

Range		Δa -SCC	da/dt
K_I	J_I		



Stress corrosion cracking of austenitic stainless ste



edge showed serrations or markings (parallel lines) perpendicular to the fracture surface (figure 7a). These serrations, almost parallel to one another, were observed at grain boundary markings. Deep grain boundary grooving and dissolution pits were observed at surfaces perpendicular to the fracture surface.

4.4d Sensitized material with prior cold work: Specimens of 304 stainless steel + sensitization showed features similar to those without sensitization. In 20% cold work + sensitized samples, the crack initiation was mainly intergranular (transgranular + intergranular) unlike transgranular initiation in non-sensitized samples.

4.4e Tests at lower temperatures: Solution annealed, solution annealed + 10% cold worked samples tested at 373 K showed similar features to those tested at 381 K. When the test temperature was lowered to 353 K, the sensitized specimens showed mainly intergranular crack initiation and propagation.

5. Discussion

The mechanism suggested for SCC of austenitic stainless steel is based on the following experimental observations in the present study:

- (i) Existence of a plateau region on crack growth curve.
- (ii) Plateau crack growth rate of the order of 10^{-8} ms^{-1} for non-sensitized samples.
- (iii) Increase in crack growth rate on sensitization and cold working.
- (iv) Existence of threshold K_{ISCC} or J_{ISCC} and their dependence on cold working.
- (v) Matching of fracture surfaces.
- (vi) Transgranular fracture features like river lines, facets and striations seen on the fracture surface.
- (vii) Discontinuous mode of fracture as revealed by arrest marks on the fracture surfaces.
- (viii) Transition in mode of fracture in the case of sensitized samples.

Stress corrosion cracking of austenitic stainless steels



increase in crack growth rate on cold work observation (table 2). However, the mechanical stress values on cold working.

As far as the surface mobility mechanism (melting point 1097 K) is formed, the crack procedure given by Galvele (1987). Stress were assumed to be present at the crack stress will be of this magnitude. The crack temperature of 381 K are shown in table 4 measured crack growth rates. It is seen that much higher than the observed ones. If are assumed to be iron halides with low growth rates would be still higher. Thus increase in crack growth rates with cold work with the present observations. The fracture crack propagation also cannot be explained is that it is speculative as the assumption

A brittle component along with anodic authors (Jones 1985; Dickson *et al* 1987; the unified mechanism of Jones (1985), by cleavage-like fracture due to the accumulation tip. The root mean distance R that the dislocation tip is given by

$$R = 2.45 (Dt)^{1/2},$$

taking t as the time per crack growth event data and a value for $D = 10^{-12}$ cm²/sec (L R which is equal to the crack growth per event sensitized and 10% cold worked material 1.3 μ m respectively. Crack arrest markings and 7a) and crack growth per acoustic event 5) show that crack growth per jump is

Stress corrosion cracking of austenitic stainless steels

Table 4. Crack growth rates calculated using the equation of Galvele (1987) (Test temperature 381 K).

Material condition	Crack growth rate (ms^{-1}) (calculated)	Crack growth rate (measured)
Solution annealed	7.6×10^{-7}	1.3×10^{-6}
Sensitized	7×10^{-7}	2.3×10^{-6}
10% Cold worked	2.6×10^{-6}	4×10^{-6}
20% Cold worked	3.7×10^{-6}	8×10^{-6}
10% Cold worked + sensitized	1.8×10^{-6}	2.3×10^{-6}
20% Cold worked + sensitized	3.1×10^{-6}	1×10^{-6}

Table 5. Acoustic data in K_I -independent region.

Material condition	K_I range ($\text{MPa}\cdot\text{m}^{1/2}$)	Average time period/event (sec)	$\Delta a/N$ ($\mu\text{m}/\text{event}$)
SA	33–46	50	0.55
SA	24–30	72	1.15
Sensitized	15–25	375	2.30
10% CW	43–80	2870	15.00
10% CW	24–43	3120	11.00

SA, solution annealed; CW, cold worked.

diffusion in austenitic stainless steels measured by the same

6. Conclusions

The main observations on the crack growth in the acidified sodium chloride solution (b) are:

- (i) Crack growth rates of the order of 10^{-8} m/cycle for the annealed material. Threshold parameters for the cold working. Sensitization and the probability of intergranular fracture.
- (ii) Fractographic features and acoustic emission characteristics of fracture.
- (iii) Activation energies for the crack growth in the range of 50 to 65 kJ/mol.

These results have been discussed in the context of a proposed mechanism involving the role of hydrogen (diffusion to the crack tip) in the brittle component of the observations in the present investigation.

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Acoustic emission behaviour during stage crack growth in an AISI type 316 austenitic steel

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Abstract. Acoustic emission (AE) behaviour during fatigue crack growth in ductile AISI type 316 austenitic stainless steel is reported. The II Paris regime of FCG could be distinguished by a change in AE activity with increase in crack growth rate. The transition point in the $\log da/dN$ plot coincides with that in the $\log da/dN$ plot. The AE activity ΔK during stage IIa and decreases during stage IIb. The major AE activity in stage IIa is found to be the plastic deformation within the cyclic plastic zone. The phenomena such as monotonic plastic zone (MPZ) expansion, crack closure, etc. The increase in AE activity with increase in crack growth rate is attributed to the increase in the size of the CPZ which is generally observed under plane strain conditions. The decrease in AE activity during stage IIb is attributed to the decrease in the size of the CPZ under plane stress conditions. The AE activity during the substage IIa is attributed to irreversible cyclic plastic deformation, multiplication and rearrangement of dislocations taking place. The AE activity is found to strongly depend on the optimum combination of CPZ, average plastic strain range and the number of cycles between crack growth increments. Based on this, an empirical relationship between the cumulative crack growth and AE activity is proposed and is found to agree well with experimentally observed data.

Keywords. Acoustic emission; ringdown counts; fatigue crack growth; AISI type 316 stainless steel.

1972; Hideo Kusanagi *et al* 1980). It has been observed that AET provides useful information for studying crack growth and giving insight into the underlying mechanisms. The feasibility of using AET for crack growth monitoring was studied by Gerberich and Hartbower (1967) and Hartbower *et al* (1968) in their investigations on AE from fatigue crack growth (FCG). They found that AET is sensitive to crack growth rates greater than 10^{-5} m/cycle which is much higher than the range of crack growth rates encountered in engineering structures. Dunegan *et al* (1968) showed a power law relationship between the number of acoustic emission events (N) resulting from the plastic deformation near the crack tip and the crack growth factor (K) as $N = AK^m$. Experimental results show that m varies from 4 to 8 for different materials. This study established that it is possible to continuously monitor slow crack growth by AE, if we can determine the constants A and m for a given material of particular thickness. Following this, several attempts have been made to use AET for studying crack growth on different materials. These studies have resulted in correlations between AE parameters such as cumulative AE rise counts (counts/cycle) with fatigue parameters such as stress intensity factor (K_I), crack growth rate (da/dn) etc (Dunegan *et al* 1970; Mori *et al* 1974; Dunegan 1974; Lindley *et al* 1978; Mori *et al* 1980; Dunegan *et al* 1981). All these investigations suggest that AET can be used as an in-service inspection method. AET, which is sensitive to dynamic changes such as plastic deformation and crack growth, is well suited for continuous monitoring of fatigue crack growth.

Many researchers have reported that the FCG behaviour consists of an initial and later parts of the linear stage II Paris curve. (Birnbaum and Edidovich 1974; Moorthy *et al* 1991). It has been observed that the FCG can be divided into two substages, IIa and IIb (Masuda *et al* 1981). Stage IIa corresponds to structure sensitive slow crack growth where a microcrack advance after a certain number of cycles. Stage IIb where crack propagation is insensitive to submicroscopic structural changes and propagates with every load cycle. Hence, a significant correlation exists between the associated acoustic emission (AE) behaviour and the crack growth expected.

occurs even at lower load level throughout the fatigue cycle. The AE generated is associated with extensive dislocation generation and rearrangement. Only the peak load AE is not likely to give information about the active AE sources which contribute to the fatigue damage mechanism. For ductile materials, the AE generated during the entire fatigue cycle is required to be acquired to get the information from all possible sources of AE. It is thought to be essential to analyze the extent of contribution of each AE source and finally to establish the main source of AE and its relation into the relationship between AE behaviour and fatigue crack growth. Authors are not aware of any such attempts reported by any one. Also, there is no study reported in the literature to analyze the AE behaviour during the two substages IIa and IIb. The objective of the present investigation is to study the AE behaviour during stage II FCG in an AISI type 316 stainless steel to establish the major source of AE during fatigue crack propagation and analyzing AE generated throughout the loading cycle. Also, to predict the relationship between the AE parameter and the crack growth factor ΔK .

2. Experimental

Nuclear grade AISI type 316 stainless steel compact tension specimens of 10 mm and 12.5 mm thicknesses and having chevron notch were prepared according to the ASTM standard E647-86 (1986). Two different thicknesses were used to study the influence of specimen thickness on the fatigue crack growth. The chemical composition of the steel is as follows: Ni: 12.43%, Cr: 18.28%, C: 0.054%, Mn: 1.69%, Si: 0.64%, S: 0.006%, P: 0.002%. The specimens were solution-annealed at 1323 ± 5 K for 1 h in vacuum (133 $\times 10^{-5}$ Nm⁻²). The average grain size of the microstructure was 10 μ m. The yield stress and ultimate tensile stress of the material were 275 and 580 MPa respectively. All the specimens were fatigue pre-cracked according to the ASTM standard E 647 (1986) in a MTS model 811 electrohydraulic test machine.

dummy test showed that the contribution from external noises such as rotating pins, grip noises etc to the recorded AE is insignificant under the experimental conditions selected. This is attributed to the low frequency of AE signals generated by these noise sources as compared to the resonant frequency of the sensor used. The AE ringdown counts (RDC) were used for correlation of AE activity with FCG behaviour. The cyclic stress intensity factor ΔK is calculated from the standard expression used for CT specimens (ASTM standard 1986). The crack growth rate (da/dn) and the cumulative RDC (N) were measured at different number of cycles (n).

3. Results and discussion

Figure 1 shows a typical plot of cumulative RDC (N) as a function of number of cycles (n) for one of the specimens. Almost negligible AE activity recorded in the initial stage (up to 50000 cycles) indicates that the interference of mechanical noise is insignificant. Figures 2a and b show the plots of $\log(da/dn)$ and $\log(N)$ as a function of $\log \Delta K$ for two specimens each in 25 mm and 12.5 mm thicknesses, respectively. The variation in $\log(da/dn)$ with $\log \Delta K$ shows a linear behaviour for all the specimens. This linear behaviour has been fitted according to the Paris equation,

$$da/dn = C(\Delta K)^m, \quad (1)$$

where C and m are constants.

The C and m values for different specimens estimated from the above equation are given in table 1. The variation in $\log(N)$ with $\log(\Delta K)$ shows a two-slope behaviour for all the specimens. This two slope behaviour indicates a change in the crack growth mechanism within the linear Paris regime, and suggest that the AE parameter like cumulative RDC can be used to distinguish the two subdivisions of the stage II crack propagation.

The presence of two substages IIa and IIb in stage II can be observed when one plots the variation in $\log(da/dn)$ with $\log(n)$ (Gurevich and Eidorich 1974). Figures 3a and b show the variation in $\log(da/dn)$ and $\log(N)$ as a function of $\log(n)$ for all the specimens. These figures show a two-slope behaviour for crack

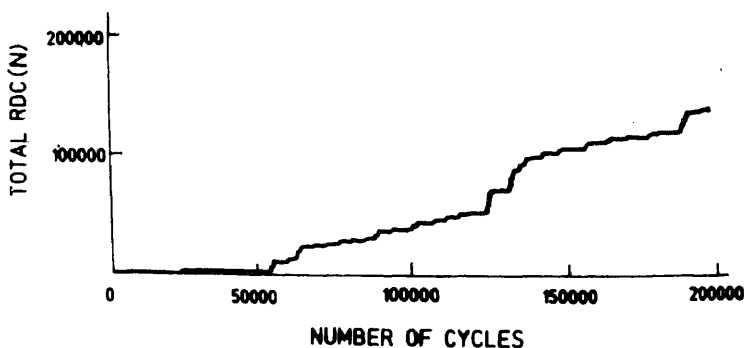


Figure 1. Typical variation of cumulative ringdown counts (N) as a function of number of fatigue cycles (n).

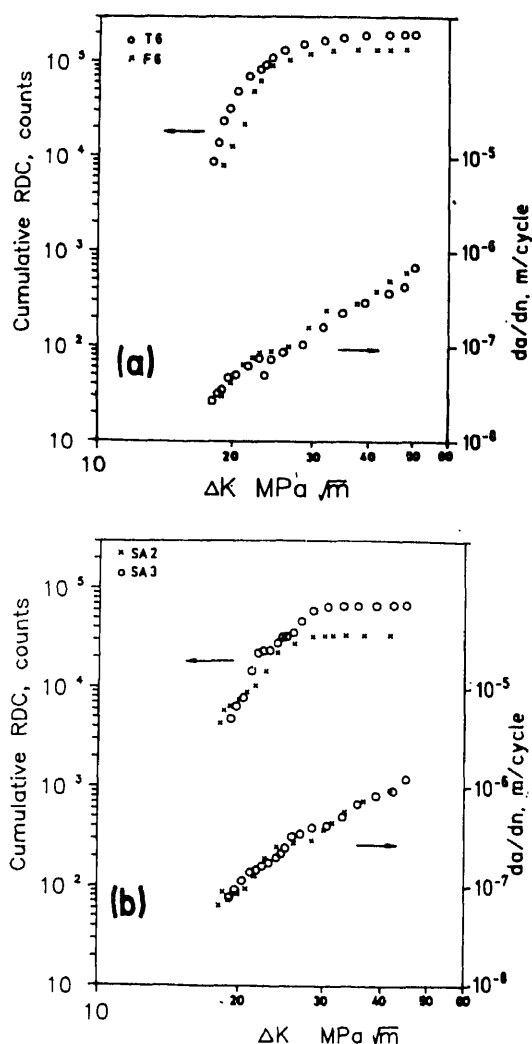


Figure 2. Variation of cumulative RDC and crack growth rate (da/dn) as a function cyclic stress intensity factor (ΔK) for (a) 25 mm and (b) 12.5 mm thick specimens.

propagation rate (da/dn) and AE cumulative RDC (N) during stage II FCG. The transition from stage IIa to IIb can be observed from the sharp increase in the slope of da/dn and a sharp decrease in AE activity after a certain number of cycles. The two slope behaviour shown by both the crack growth rate and AE activity itself is a direct evidence for a two-stage fatigue process during stage II. Some of the earlier studies (Morton *et al* 1973; Paul McIntire 1987) showed a linear relationship between AE count rate (counts/cycle) and ΔK . This may be due to collection of only peak load AE activity. Dunegan *et al* (1974) and Ohira

et al (1980) observed a transition in peak load AE activity over a small range of ΔK in aluminium and steel and the same was attributed to the stress state change from plane strain to plane stress. Dunegan *et al* (1974) also showed that, after the transition, again AE activity increases as the ΔK increases. This occurs even though the plane stress condition dominates at higher ΔK . They could not explain the presence of this transition behaviour over a small ΔK range. Ohira *et al* (1980) attributed the high AE activity at lower ΔK to fracture events induced by the triaxial state of stress under plane strain condition. This explanation does not fully explain the scenario as the fracture events can also occur at higher ΔK . In fact, the crack growth rate sharply increases only under plane stress condition at higher ΔK . Also, the tensile deformation study on stainless steel using AET, reveals that the events like microvoid coalescence and microcrack growth occurring during necking process under triaxial state of stress do not generate detectable AE signals (Baldev Raj and Jayakumar 1991). In none of the FCG studies reported, the transition in AE behaviour was correlated in detail with the crack growth behaviour. In this study, an attempt has been made to relate the transition in AE behaviour with that of crack growth behaviour in the AISI type 316 stainless steel.

3.1 Transition from stage IIa to IIb

The coordinates for the transition point for changeover from stage IIa to IIb are given by the following two equations (Tanaka *et al* 1981):

$$\Delta K_0 = 10 Eb^{1/2}, \quad (2)$$

$$(da/dn)_0 = 10^3 b, \quad (3)$$

where ΔK_0 is the stress intensity at transition in $\text{MPa}\sqrt{\text{m}}$, E the Young's modulus in MPa and b the Burger's vector in m and $(da/dn)_0$ the crack growth rate at transition in m/cycle.

The values of ΔK_0 and $(da/dn)_0$ for AISI type 316 stainless steel, predicted from the above equations using $E = 193 \text{ GPa}$ (ASM Handbook 1968) and $b = 2.5 \times 10^{-10} \text{ m}$, are $30.5 \text{ MPa}\sqrt{\text{m}}$ and $2.5 \times 10^{-7} \text{ m/cycle}$ respectively which are close to the observed values as shown by table 2. The transition from stage IIa to IIb has been observed to occur in this material when the crack growth rate reaches a value of $\sim 10^{-7} \text{ m/cycle}$ which is in general agreement with the reported crack growth rate values at the transition (Grinberg 1982, 1984).

Table 1. Fatigue constants C and m for different specimens.

Specimen No.	Thickness (mm)	Fatigue constants	
		m	C
T6	25	2.82	9×10^{-12}
F6	25	2.92	8×10^{-12}
SA2	12.5	3.26	6×10^{-12}
SA3	12.5	3.01	1.3×10^{-11}

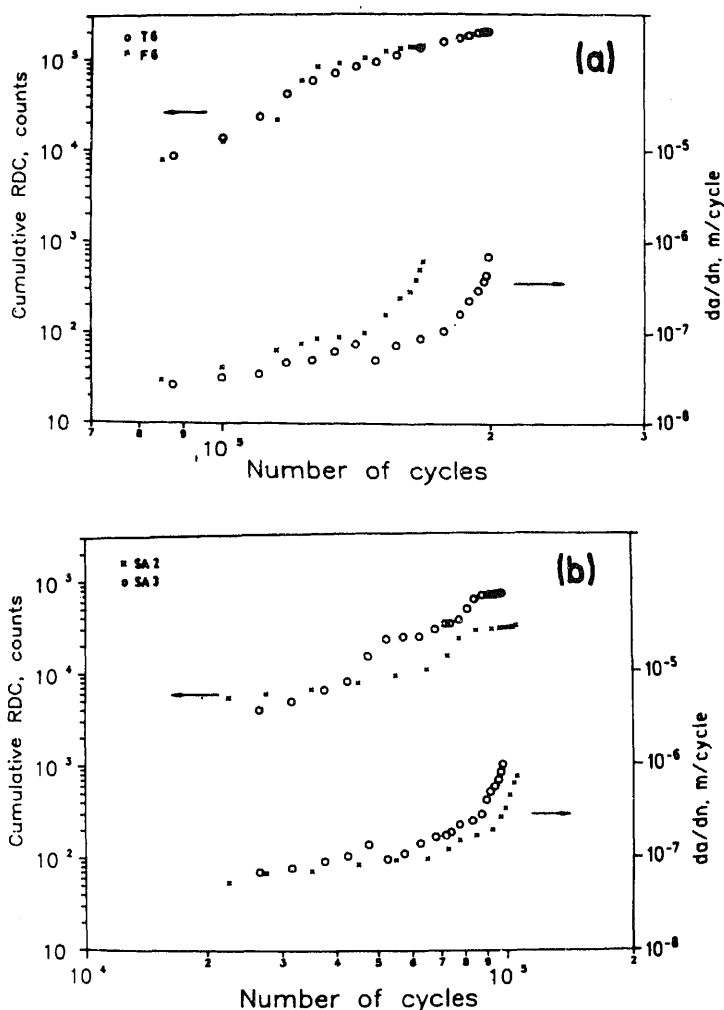


Figure 3. Variation of cumulative ringdown counts (N) and crack growth rate (da/dn) as a function of number of fatigue cycles (n) for (a) 25 mm and (b) 12.5 mm thick specimens.

The transition shown by the plots $\log(N)$ vs $\log(n)$ matches with that of $\log(da/dn)$ vs $\log(n)$ plot. Therefore, it can be reliably concluded that AET can be utilized for identification of the transition from stage IIa to IIb using $\log(N)$ vs $\log(n)$ plot during structural integrity monitoring applications where obtaining crack growth information is difficult in order to use the $\log(da/dn)$ vs $\log(n)$ plot. The information on AE signals thus greatly helps in recognizing the transition essential for assessing the fatigue damage.

Figures 4a and b show the log-log plots for variation in the RDC generated per unit crack extension ($\Delta N/\Delta a$) with cyclic stress intensity factor ΔK for different specimens. $\Delta N/\Delta a$ was calculated by dividing the ringdown counts between two adjacent crack length measurements by the corresponding increment in the crack

Table 2. Observed values of transition coordinates $(\Delta K)_0$ and $(da/dn)_0$ for different specimens.

Specimen No.	Thickness (mm)	ΔK_0 (MPa $\sqrt{m}$)	$(da/dn)_0$ (m/cycle)
F6	25	29.24	2.4×10^{-7}
T6	25	28.05	2.25×10^{-7}
SA2	12.5	28.16	3.7×10^{-7}
SA3	12.5	30.39	3.08×10^{-7}

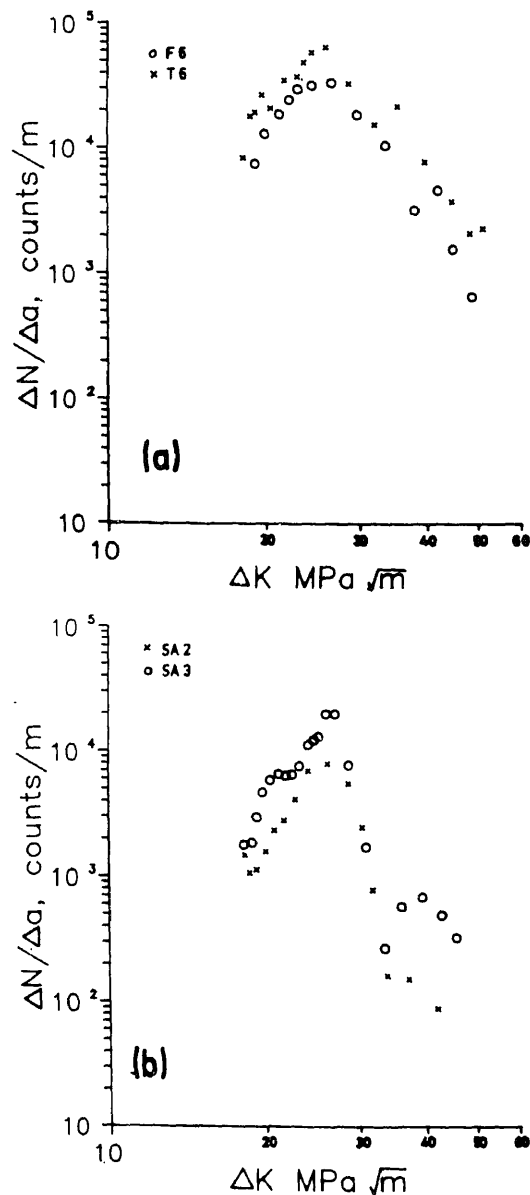


Figure 4. Variation of ringdown counts per unit extension of crack length ($\Delta N/\Delta a$) as a function of cyclic stress intensity factor (ΔK) for (a) 25 mm and (b) 12.5 mm thick specimens.

length. $\Delta N/\Delta a$ goes through a maximum with increase in ΔK indicating a transition. These plots also suggest that the $\log(N)$ vs $\log(\Delta K)$ plots in figures 2a and b appear flat during stage IIb due to the logarithmic scale selection. It should be noted that significant AE is generated even during stage IIb. But, contrary to the sharp increase in da/dN there is a decrease in the rate of increase in N after the transition point for all the specimens. This implies that the mechanism responsible for stage IIa gives higher AE as compared to the mechanism responsible for stage IIb. In order to understand this difference in AE behaviour, it is necessary to discuss the mechanisms of FCG and identify the major source of AE.

According to Laird-Smith (1967) model, FCG during stage II occurs by crack tip blunting and resharping mechanism during loading and unloading part of the fatigue cycle respectively. The crack growth mechanism is associated with plastic deformation, crack closure and crack jump near the crack tip. All these phenomena can contribute to AE. In order to establish a better relationship between FCG behaviour and the AE behaviour, it is necessary to find out the major source of AE among these.

3.2 Mechanisms of fatigue crack growth

It has been observed that during the early part of stage II, each striation is formed not in one but in several loading cycles as against matching striations with number of loading cycles in the later part of stage II (Grinberg 1984). This difference in FCG behaviour has been explained by the following two mechanisms taking place in the early part (stage IIa) and later part (stage IIb) of stage II.

3.2a FCG mechanism during stage IIa: The effective stress intensity, K_{eff} at the crack tip is given by

$$K_{\text{eff}} = K_{\text{max}} - K_{\text{ex}}, \quad (4)$$

where K_{max} is the stress intensity at maximum load, P_{max} and K_{ex} the stress intensities needed for crack extension.

For crack to extend, $K_{\text{eff}} > 0$. Even in tension-tension fatigue cycle, compressive stresses are generated at the crack tip due to the displacement/stress field associated with the dislocations (Louat *et al* 1993). The region with compressive stress is known as reversed plastic zone or cyclic plastic zone (CPZ) (Suresh 1991). During stage IIa, because of presence of compressive stress at the crack tip, $K_{\text{max}} < K_{\text{ex}}$ and $K_{\text{eff}} < 0$. Therefore, crack is unable to extend in the immediate next loading cycle. With progressive fatigue cycles, the compressive stress at the crack tip decreases slowly and becomes tensile after certain number of cycles. At this stage, the K_{eff} becomes > 0 , thus enabling the crack to extend in the subsequent loading cycle.

3.2b FCG mechanism during stage IIb: At the transition point from stage IIa to IIb, the monotonic plastic zone size (MPZ) increases sharply. This results in microplastic instability produced by change in the degree of plastic constraint, i.e.

from plane strain to plane stress condition. Under this condition, $K_{\max}$ is sufficiently larger than K_{ex} and hence, the crack growth is essentially controlled by $K_{\max}$ value. The compressive stress at the crack tip can easily be overcome during loading part of each cycle and therefore crack extension occurs in each cycle (Grinberg 1984). Hence, the crack growth rate sharply increases during stage IIb.

3.3 Various sources of acoustic emission during fatigue crack propagation

3.3a Ductile crack extension as a source of AE: If the crack jump is considered as the main source of AE, the cumulative RDC (N) vs ΔK plot would have shown a linear relationship during entire stage II regime. But during stage IIb, the AE activity decreases (figure 4). If we calculate the minimum crack extension for a detectable AE signal to be emitted by a microcrack for a stainless steel, according to the theory suggested by Scruby *et al* (1981), it would be approximately $1 \mu\text{m}$. It is generally observed that for iron and steels, the striation spacing is less than $0.5 \mu\text{m}$ for $da/dN < 10^{-7} \text{ m/cycle}$ (Roven *et al* 1991) which is smaller than minimum needed for generating detectable AE. Pickard *et al* (1975) also had observed that the microcrack growth rate in AISI 316 SS is $\approx 0.52 \mu\text{m/cycle}$ at $\Delta K \approx 28 \text{ MPa}\sqrt{\text{m}}$. The fracture process is found to occur within the process zone near the crack tip. The length of the process zone in the direction of crack propagation is given by (Moura Branco *et al* 1989),

$$R_{\text{pz}} = \Delta K^2 / 8E \sigma_{\text{yc}} \quad (5)$$

where σ_{yc} is the cyclic yield stress.

From the above equation, the size of the process zone itself is $\approx 1 \mu\text{m}$ at $\Delta K \approx 25 \text{ MPa}\sqrt{\text{m}}$ and the number of cycles required for the complete failure of the process zone is few tens of cycles. Hence, the crack extension at any instant is expected to be much smaller than $1 \mu\text{m}$ during stage IIa. Therefore, it is inferred that ductile crack growth process does not generate detectable AE during stage IIa. However, it has the possibility to contribute to AE activity at higher ΔK during stage IIb.

3.3b Crack closure as a source of AE: Generally, the crack closure phenomenon is observed to be dominant near the threshold and stage I FCG regions. Its effect is less pronounced during stage II propagation under mode I loading condition. The plasticity induced crack closure is considered essentially as a plane stress effect (Arthur McEvily 1988) and its effect can be observed under plane strain only when the R ratio approaches zero. During stage IIa, the major portion of the thickness is under plane strain condition. Hence, this type of closure is only a surface phenomenon. Recently, Louat *et al* (1993) have shown from an analytical estimation using dislocation theory that the plasticity induced crack closure cannot occur during unloading part of the cycle. Asperity or roughness induced crack closure results from the mismatch between the two crack surfaces during unloading (Arthur McEvily 1988). This is promoted by low ΔK when the size of the process zone is less than the grain size and in presence of microstructure consisting of coarser grains, shearable and coherent precipitates (Suresh 1991). In this study, a nuclear grade

316 stainless steel with almost negligible inclusion content was used under solution treated condition. Therefore, the contribution from this roughness induced crack closure is likely to be absent or negligible. The lower AE activity at the early part of the fatigue cycling (figure 1) also clearly supports the fact that the influence of crack closure on AE is not significant in the present study. It is clear from the above discussions that the ductile crack extension or the crack closure are not likely to be the major sources of AE during stage II FCG. Hence, the plastic deformation near the crack tip as a major source of AE needs serious consideration.

3.3c Plastic deformation as a source of AE: It has been suggested that spontaneous dislocation generation (Rice and Thompson 1974), and higher mobility of the dislocations (Neumann *et al* 1979) near the crack tip leads to the crack tip blunting and subsequent crack propagation in a ductile manner. Thus, crack propagation is highly sensitive to dislocation mechanism that is occurring near the crack tip region. The plastic deformation zone ahead of a fatigue crack can be divided into three regions (Guerra Rosa *et al* 1984): (i) monotonic plastic zone (MPZ), (ii) cyclic plastic zone (CPZ) which lies within the MPZ, and (iii) process zone or crack tip opening displacement (CTOD) affected zone within the CPZ.

(i) *Monotonic plastic zone as a source of AE:* Under both plane stress and plane strain conditions, the size of the MPZ is proportional to the square of ΔK under fatigue loading (Suresh 1991). Therefore, if the deformation in the MPZ is considered as the main source of AE, the AE activity should increase with increase in ΔK even during stage IIb like that observed in stage IIa. However, it is observed experimentally during the present study that the RDC per unit crack extension decreases ($\Delta N/\Delta a$) with increase in ΔK during stage IIb (figure 4). The deformation in the MPZ can be considered to obey the Kaiser effect (Palmer 1973), i.e. the AE can be generated only from the region where the stress value increases over previous value due to the crack extension. Therefore, the AE activity from the MPZ expansion can arise only from a thin zone at the elastic-plastic boundary. But in FCG of metals, even during stage IIb at a crack growth rate of $1 \mu\text{m}$ per cycle, the increment in the size of MPZ after each crack extension (a) is less than $1 \mu\text{m}$ and hence, is too small to generate detectable AE. In addition, during stage IIa of FCG, since, crack growth is not expected to occur in each cycle, the MPZ expansion does not occur in each loading cycle. Therefore, the occurrence of higher AE activity in stage IIa as compared to stage IIb indicates that the MPZ expansion may not be the major source of AE during FCG.

(ii) *Cyclic plastic zone as a source of AE:* In FCG process of metallic materials, cyclic plasticity is supposed to occur only within CPZ (Moura Branco *et al* 1989). An element in the material within this zone is subjected to hysteresis loops similar to those observed in a low cycle fatigue test. The size of the CPZ is given as (Guerra Rosa *et al* 1984),

$$R_{\text{cpz}} = \alpha_c (\Delta K / \sigma_{ys})^2, \quad (6)$$

where σ_{ys} is the monotonic yield stress and α_c is the coefficient of CPZ. As a source volume of AE, the size of the CPZ is much larger than the crack growth

area, crack closure area and the increment in the MPZ volume after each crack jump. Earlier studies (Hahn *et al* 1972; Guerra Rosa *et al* 1984) have shown that, in the Paris regime of FCG, the CPZ generally experiences strain cycles with plastic strain range between 10^{-3} and 10^{-1} . Eventhough the size of the CPZ is smaller than the size of the MPZ, the cyclic plasticity within the CPZ occurs during each cycle and is associated with extensive dislocation generation and rearrangement. There is a continuous dislocation substructure development within the CPZ associated with the variation in the cyclic saturation stress and the plastic strain range. The substructure evolution with increasing number of cycles is well investigated by Roven and Nes (1991). The substructure evolution occurs in various stages from the CPZ boundary to crack tip: first the development of dislocation walls and veins near the CPZ boundary, then to a labyrinth structure, dislocation cells inside the CPZ and finally to banded cells and subgrains in the regions close to the crack tip. This involves extensive dislocation mobility within the CPZ. Tensile deformation study on cold worked AISI 316 stainless steel has shown that the deformation in the presence of the dislocation substructure generates higher AE activity as compared to a solution annealed material during pre-yield deformation (Moorthy *et al* 1994). It has been observed that the pre-yield AE activity increases with increase in percentage prior to cold work. This behaviour has been explained using the composite deformation model applied for the deformation of dislocation substructure. Therefore, dislocation substructure deformation during the cyclic plasticity within the CPZ could be a major source of AE during FCG.

3.4 AE behaviour during stages IIa and IIb

It is observed from figures 2 and 4 that the AE activity increases with increase in ΔK during stage IIa and decreases during stage IIb. The detailed discussions made earlier point towards the interpretation that CPZ could be a major source of AE during FCG in this material. It has been observed that the CPZ in a FCG process is always generated and developed under plane strain conditions (Moura Branco *et al* 1989). The measurements of CPZ sizes using etching technique in Fe-3%Si steel (Hahn *et al* 1972) and that using microhardness technique in medium strength steel (Guerra Rosa *et al* 1984) have indicated that the coefficient of CPZ size α_c has larger value under plane strain conditions than that under plane stress conditions. The size of CPZ computed from the effective strain range distribution in aluminium alloy (Davidson and Lankford 1983) has also indicated that the size of the CPZ decreases with increase in ΔK under plane stress condition. Therefore, for a given ΔK , the size of the CPZ under plane strain condition is larger as compared to that under plane stress condition.

During stage IIa, the plane strain condition dominates the major portion of the specimen thickness. As the coefficient of CPZ size increases under plane strain condition, the net volume of the CPZ is expected to increase with ΔK . Hence, the AE activity increases during stage IIa. The plane stress condition dominates when the size of the monotonic plastic zone becomes greater than one fourth of the specimen thickness (Hamel *et al* 1981; Grinberg 1984). This occurs at $\Delta K \approx 30 \text{ MPa}\sqrt{\text{m}}$ for the stainless steel specimens studied by us. The transition from stage IIa to IIb also occurs around the same ΔK value. Due to decrease in

the coefficient of CPZ size under plane stress condition, the increment in volume of the CPZ cannot be large enough to emit significant AE. The size of the CPZ would also decrease with increase in ΔK under plane stress conditions as observed by Davidson and Lankford (1983). In addition, the plastic strain range in CPZ increases at higher ΔK values (Roven and Nes 1991). It is also known that as the crack length increases, strain intensification occurs in the plastic zone (Navarro and De Los Rios 1992). Therefore, the mobility and mean free path of the dislocations are much reduced at higher ΔK . Hence, there is a reduction in the extent of cyclic plasticity. As a result, the AE activity is expected to decrease during stage IIb. It can thus be concluded that the AE behaviour during stage II FCG depends to a significant degree on the increment in the size of CPZ and the strain range within CPZ.

According to cumulative damage theory of FCG, the material near the crack tip strain hardens progressively with number of cycles until the stress at the crack tip reaches a critical value for crack extension (Davidson and Lankford 1983). The strain hardening near the crack tip region mainly occurs by cyclic deformation. It is also observed that the number of cycles required for each crack extension decreases with increase in ΔK (Roven and Nes 1991). This is due to the fact that the plastic strain range at the crack tip is strongly dependent on ΔK and therefore, more number of cycles are required to attain the critical strain for crack extension at lower ΔK . Therefore, during stage IIa, we can expect that more energy is dissipated by the cyclic plasticity which results in more AE activity. Since, strain intensification occurs progressively in the plastic zone as the crack length increases, the critical strain near the crack tip can be reached in each cycle during stage IIb. At higher ΔK , the crack growth is essentially controlled by $K_{\max}$ value. Therefore, the energy dissipation by plastic deformation is reduced and hence, the AE activity also decreases. From the above discussions, it becomes obvious that AE during FCG strongly depends on the size of CPZ, the plastic strain range and the number of cycles required for each crack extension.

3.5 An empirical model to relate AE and ΔK during stage IIa

Detectable AE activity is generated only in the presence of substantial dislocation mobility, which exists under the condition of optimum plastic strain range (of the order of 10^{-3} to 10^{-2}). Very low as well as very high strain could not generate detectable AE due to reduced dislocation mobility. The cyclic plasticity occurs with the cyclic strain range of 10^{-3} to 10^{-1} (Guerra Rosa *et al* 1984). The optimum combination of volume of CPZ and the plastic strain range to generate significant AE prevails only during stage IIa. Therefore, AE RDC generated at a given ΔK before each crack jump should depend on the product of volume of CPZ and the plastic strain range with which the cyclic plasticity occurs. Since, the number of cycles required to attain critical strain for crack extension is a function of ΔK , AE RDC generated at given ΔK can be assumed to be proportional to the number of cycles required before each crack extension.

The volume of CPZ is given as

$$V_{\text{cpz}} = \pi * R_{\text{cpz}}^2 * B, \quad (7)$$

$$V_{cpz} = \pi * B * \alpha_c^2 * (\Delta K / \sigma_{ys})^4, \quad (8)$$

where R_{cpz} is the radius of CPZ, α_c the coefficient of CPZ size, B the thickness of the specimen and σ_{ys} the yield stress.

The plastic strain range within the CPZ is given as (Jacques Lantegne and Jean Paul-Bailon 1981)

$$\Delta \epsilon_p = \frac{0.4 (1 - \nu^2) \Delta K^2}{\pi \sqrt{3} \cdot c \cdot x \cdot \sigma_{ys} \cdot E}, \quad (9)$$

where x is the distance from the crack tip, c is a triaxiality factor, ν the Poisons' ratio and σ_{ys} the monotonic yield stress. Eventhough the plastic strain range is a function of the distance from the crack tip, as a simplification, we assume that this is an average plastic strain range.

Let us assume that each crack jump occurs by complete rupture of the process zone. The number of cycles required for the failure of the process zone is given by

$$N_f = R_{pz} / (da/dn), \quad (10)$$

where, R_{pz} the size of the process zone is given by (5).

It follows that the number of RDC generated by the cyclic plasticity before the next crack jump is given as

$$N \propto (V_{cpz} * \Delta \epsilon_p) * N_f. \quad (11)$$

Substituting for V_{cpz} , $\Delta \epsilon_p$ and N_f from (8), (9) and (10) respectively, we get,

$$N \propto (\Delta K^4 * \Delta K^2) * \Delta K^2 / (da/dn). \quad (12)$$

Considering that $da/dn \simeq C \Delta K^3$ for this material (table 1),

$$N \propto \Delta K^5. \quad (13)$$

The crack propagation process can be considered as a cumulative growth process due to incremental increase in crack length. After each crack jump, there is an increment in ΔK . It represents only the cumulative effect. The increment in ΔK gives rise to an increment in the volume of CPZ and hence, an increment in AE counts. Therefore, it is more appropriate to relate the cumulative AE ringdown counts with ΔK . As already mentioned, the number of cycles required for each crack extension is more than one during stage IIa and is equal to one during stage IIb. Therefore, for a given increment in crack length, the counts per cycle will always give lower value during stage IIa as compared to stage IIb. Hence, counts/cycle is not an appropriate parameter. According to (13), during stage IIa, the plot of cumulative RDC vs ΔK should show a slope of 5. Since, the transition from stage IIa to IIb is found to occur at $\sim \Delta K = 30 \text{ MPa}\sqrt{m}$. The data up to $\simeq 30 \text{ MPa}\sqrt{m}$ have been considered for the calculation of the slope and is shown

in figures 5a and b for all the samples. The value of the slope and the correlation coefficient of the best fit for different samples are shown in table 3. There is a good agreement between the experimentally observed values and the predicted value of the exponent in (13). Even when we consider the statistical behaviour of AE activity, the correlation coefficient indicates that the fit is reasonably good.

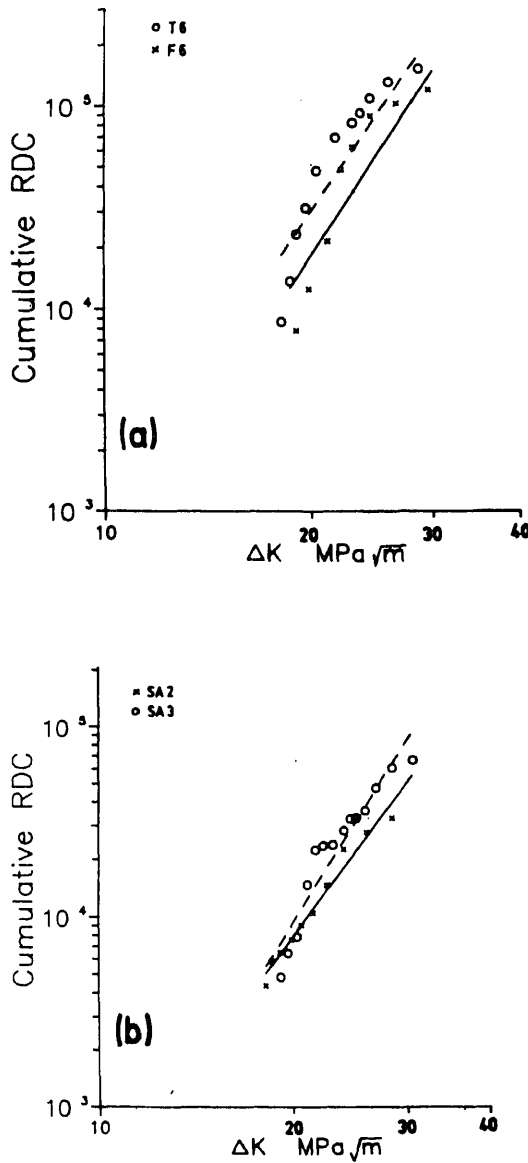


Figure 5. Variation of cumulative ringdown counts (N) as a function of cyclic stress intensity factor (ΔK) during stage IIa FCG for (a) 25 mm and (b) 12.5 mm thick specimens.

Table 3. The slope of log cumulative RDC vs log ΔK plot during stage IIa for different samples.

Specimen No.	Thickness (mm)	Slope of cumulative RDC vs ΔK plot	Correlation coefficient
T6	25	4.99	0.83
F6	25	5.22	0.81
SA2	12.5	4.54	0.97
SA3	12.5	5.39	0.90

4. Conclusions

Acoustic emission technique has been used for detecting the transition from stage IIa to IIb in the Paris region. As there is no need for crack growth measurement for determining the transition, use of AET during structural integrity monitoring can effectively predict the sharp increase in crack growth rate and ensures avoidance of catastrophic failures. Among the various possible sources of AE, detailed discussions presented in this paper have established that the cyclic plasticity within the cyclic or reversed plastic zone is the main source of AE during FCG. Considering AE activity dependence on the volume of cyclic plastic zone and the plastic strain range, it has been predicted as well as experimentally observed that the cumulative RDC is proportional to the fifth power of ΔK during stage IIa.

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A unified approach to complex crystalline and so-called quasicrystalline phases in aluminium alloys*

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Abstract. Recent developments in the complex and controversial, but fertile and fascinating field of aluminium-transition metal alloys are reviewed with particular reference to the so-called quasicrystalline phases and their rational approximants. Pauling's several approaches to icosahedral phases on the basis of twinning in cubic crystals with large unit cells are described and examined along with the difficulties in checking the structures proposed by him. A new unified crystallographic approach is presented by the author, starting with icosahedral atomic clusters in concerned alloy melts, and it is shown that this integral approach leads to a reasonably good understanding of the interrelationship between the numerous known solid phases in aluminium alloys, including icosahedral phases, decagonal phases and their rational approximants.

Keywords. Complex crystalline phases; quasicrystalline phases; aluminium alloys.

1. Introduction

Aluminium (Al) is today commercially the second most important metal in the world, even though a rather distant second to iron (Fe) which accounts for over 90% of the global annual output of metals and alloys. The tremendous technological importance of aluminium stems from its lightness, high electrical and thermal conductivity, excellent corrosion resistance, easy workability and attractive mechanical properties on alloying. No wonder, therefore, that aluminium alloys have been under study by chemists, crystallographers and metallurgists for many decades now. It became clear even by the fifties of this century (Bland 1958) that the crystal structures of intermetallic phases based on aluminium tend to be complex with much larger unit cells than associated with metals and alloys in general. The Frank-Kasper phases, e.g. $(\text{AlZn})_{49}\text{Mg}_{32}$ and $\text{Al}_6\text{Mg}_4\text{Cu}$, with 162 atoms in the unit cell, and Samson's Al_3Mg_2 phase with 1168 atoms in the unit cell have attracted special attention in this regard (see Shoemaker and Shoemaker 1988). Apart from these thermodynamically stable, equilibrium phases, a number of metastable, non-equilibrium phases including metallic glasses (see Anantharaman 1984) could be produced by rapid solidification (see Anantharaman and Suryanarayana 1987) in binary and ternary aluminium alloys during the last three decades. All these phases were amorphous or crystalline and the atomic arrangements in them could be explained and understood in terms of traditional ideas and concepts developed during the first half of this century on the structure of solids.

However, the scientific world was in for a great surprise almost exactly a decade ago when a team of Israeli, French and American investigators (Schechtman *et al*

*DEDICATED TO THE MEMORY OF PROFESSOR LINUS PAULING (1901–1994).

1984) reported on the occurrence of crystallographically forbidden five-fold diffraction symmetry in rapidly solidified Al-Mn alloys. These researchers asserted in their report that the X-ray diffraction pattern from this icosahedral phase, made up of a few strong and medium and very many weak and very weak reflections, 'could not be indexed to any Bravais lattice' and further, multiple twinning capable of explaining the observed icosahedral symmetry was ruled out on the evidence of 'dark-field images from any reflection' illuminating 'in all cases the whole grain' in electron micrographs. These bold assertions were received enthusiastically and accepted readily by most physicists and chemists interested in structural problems without any critical examination or comprehensive debate of the complex metallurgical issues involved. Thus began what looked like a new and exciting era in solid-state sciences based on the fascinating and novel paradigm of 'quasicrystallinity', postulated a little earlier for a possible new species of solids (Levine and Steinhardt 1984) through three-dimensional analogs of Penrose tiling (Mackay 1982). Concept after concept, model after model, review after review, conference after conference, book after book—all followed in quick succession, accounting for over 3000 papers on the quasicrystal phenomenon from all parts of the globe in less than a decade! All the same, despite the intense research efforts, often multi-institutional and multi-national, on the part of numerous physicists, mathematicians and materials scientists, all directed towards a few dozen icosahedral and decagonal phases (see table 1), most of them metastable and produced by rapid solidification of aluminium-transition metal (Al-TM) binary and ternary alloys, the exact atomic arrangement has not been established to this day for any one of these exotic phases on the basis of quasicrystallography.

A new dimension was added to the quasicrystal saga in 1988 with the production of thermodynamically stable quasicrystalline phases by normal cooling from the melt, like the Al-Cu-Fe, Al-Cu-Ru and Al-Pd-Mn icosahedral phases, as also the

Table 1. Approximate compositions of typical icosahedral and decagonal phases based on aluminium.

Icosahedral phases	Decagonal phases
$\text{Al}_{82}\text{Mn}_{18}$	$\text{Al}_{80}\text{Mn}_{20}$
$\text{Al}_{85}\text{Cr}_{15}$	$\text{Al}_{78}\text{Co}_{22}$
$\text{Al}_{86}\text{Fe}_{14}$	$\text{Al}_{80}\text{Ni}_{20}$
$\text{Al}_{80}\text{Ru}_{20}$	$\text{Al}_{80}\text{Pt}_{20}$
$\text{Al}_{80}\text{V}_{20}$	$\text{Al}_{80}\text{Os}_{20}$
$\text{Al}_{78}\text{Re}_{22}$	$\text{Al}_{80}\text{Fe}_{20}$
$\text{Al}_{60}\text{Li}_{30}\text{Cu}_{20}$	
$\text{Al}_{62}\text{Cr}_{19}\text{Si}_{19}$	$\text{Al}_{79}\text{Mn}_{19}\text{Fe}_2$
$\text{Al}_{73}\text{Mn}_{21}\text{Si}_6$	$\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$
$\text{Al}_{60}\text{Ge}_{20}\text{Mn}_{20}$	$\text{Al}_{65}\text{Cu}_{20}\text{Co}_{15}$
$\text{Al}_{70}\text{Fe}_{20}\text{Ta}_{10}$	$\text{Al}_{75}\text{Cu}_{10}\text{Ni}_{15}$
$\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$	$\text{Al}_{60}\text{Cu}_{25}\text{Co}_{15}$
$\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$	$\text{Al}_{63}\text{Cu}_{17.5}\text{Co}_{17.5}\text{Si}_2$
$\text{Al}_{65}\text{Cu}_{20}\text{Os}_{15}$	

Al-Cu-Co and Al-Cu-Co-Si decagonal phases, all of them displaying extremely sharp X-ray and neutron reflections, as would be expected of normal annealed crystalline metals (see Steurer 1990). The availability of single crystals of these phases has facilitated high-resolution studies using powerful synchrotron radiation during the last few years (Motsch *et al* 1992; Fettweis *et al* 1993). However, these studies have only thrown up further questions concerning the very validity of the quasicrystalline concept. As conceded recently by an acknowledged leader of the quasicrystallography school (Janot 1993) 'quasicrystallography has not yet reached the level of structure refinement that is currently reported in regular crystallography. Also the description of the structure though very easy in its high-dimensional periodic image, is not that straightforward when one deals with the three-dimensional physical atomic arrangements'. Further, as highlighted by two other strong advocates of quasicrystallography (Goldman and Kelton 1993), a second fundamental and ticklish issue has arisen, relating to 'the limits of our ability to distinguish through experiment between quasicrystals and multiply-twinned crystals with large unit cells'. Yet another significant development has been the discovery, one after the other, of many so-called rational crystalline approximants of quasicrystalline phases, which show pseudo-five-fold symmetry and are very difficult to distinguish and differentiate from the corresponding icosahedral or decagonal phases (Liu 1993; Anantharaman 1994).

2. Crystallinity and icosahedral motifs

Shortly after publication of the above-referred first report on the Al-Mn icosahedral phase alternative crystallographic approaches to these phases were advocated independently by Field and Fraser (1985), Carr (1985) and Pauling (1985). Multiple twinning or icosatwinning was implicit in all these approaches and not surprisingly, while striking a sympathetic chord among the crystallographic community (Shoemaker and Shoemaker 1988), they drew emotionally surcharged and aggressively adverse comments—dead cat and thriving pigeons!—from the pioneers of quasicrystallography (Bancel *et al* 1986; Cahn *et al* 1986; Mackay 1986). By the late eighties, despite reservations from chemists and metallurgists, the condensed-matter physicists and mathematicians seemed to have made their choice overwhelmingly in favour of the new quasicrystal paradigm (Shoemaker and Shoemaker 1988) revolving round jargons like six-dimensional space, strip projection, a-periodicity, Fibonacci sequence, phason strain etc as also models like three-dimensional Penrose tilings, random packing of icosahedral clusters, icosahedral glasses, entropic quasicrystals etc. All the same, the traditional crystallographic framework was invoked repeatedly and developed further by Pauling (1987a,b,c, 1988a–d, 1989a,b, 1990, 1991) and the present author (Anantharaman 1987, 1988a,b, 1989, 1990, 1993, 1994), chemist and metallurgist respectively, despite a uniform and persistent tendency on the part of most quasicrystallographers to ignore any suggestion of a possible crystallographic solution to this problem.

It is necessary to record in this context that chemists and metallurgists have known for some decades now that local icosahedral arrangements of atoms are possible and, in fact, do occur in a large number of inter-metallic phases, particularly in Al-TM alloys. Such icosahedral groupings have local and approximate icosahedral

symmetry. It should be clear to any one familiar with the whole field of complex crystalline phases based on aluminium, particularly those containing transition metals with smaller atoms than those of the base metal, that icosahedral groups and linkages thereof are bound to constitute important features of the new quasicrystalline phases as well. Support to this view is lent by two facts viz. some icosahedral phase compositions are the same (e.g. Frank-Kasper phases) or approximately the same as the compositions of known crystalline alloys and there are generally striking correspondences between the two in observed diffraction intensities (Shoemaker and Shoemaker 1988). In fact, even quasicrystallographers must surely have caught glimpses of what strikes any impartial observer as some sort of basic unity that underlies and connects up different phases displaying ideal or distorted icosahedral motifs.

As early as in 1987 the present author made the following concluding observations in a keynote address at the Beijing International Conference on Quasicrystals: 'An important consideration here is the close inter-relationship between the liquid, glassy quasicrystalline and in some cases even crystalline (e.g. Frank-Kasper) phases in some alloy systems. Obviously a unified approach is called for that can explain this closeness in atomic arrangements between three or four different phases with the same alloy composition. If icosahedral clusters or chains do exist in metallic liquids—the evidence so far seems to be in favour—they will have to be the starting point in model making' (Anantharaman 1987). Starting from 1988, Pauling has been referring in his papers to a 'unified structure theory' for crystalline and quasicrystalline phases based on icosahedral atomic clusters that 'can be expected to be present in molten alloys' made up of two or more metallic elements with different atomic radii (Pauling 1988a-d, 1989a,b).

An attempt is made in this paper to look for and identify the unifying link, the golden thread, as it were, that connects different Al-TM phases, with the author's model for quasicrystalline phases and their rational approximants (Anantharaman 1993, 1994) serving as a possible starting point for the quest.

3. Quasicrystals or complex crystals?

An objective assessment of the facts and findings enumerated above is bound to lead to the conclusion that the time has definitely come for the scientific community to compare comprehensively and evaluate critically the quasicrystalline and crystalline approaches to icosahedral and decagonal phases in aluminium alloys. As recorded above, the extreme complexity and unusual features of many equilibrium phases in Al-TM systems have been known and recognized as such by crystallographers for nearly half a century. These phases generally feature prominent layers or configurations of transition metal atoms, the latter generally avoiding each other in ternary and quaternary phases (Bland 1958). They also display a zone of strong X-ray reflections corresponding to interplanar spacings of about 0.2 nm, around where the 111- and 200-reflections of aluminium occur. As for non-equilibrium phases of these alloy systems, produced generally by rapid quenching of metallic melts, they are characterized by complexity of structure, twinning, stacking faults, small domain sizes etc (Anantharaman *et al* 1977). Unfortunately, most quasicrystallographers have not paid sufficient attention to the abundant

crystallographic structural data that have thus been amassed over decades for aluminium alloys of compositions similar or related to those of the new quasicrystalline phases.

Over the years Pauling and the present author have drawn the attention of the scientific community to several experimental facts which are not explained by or go contrary to the quasicrystallographic approach to icosahedral phases:

(i) Much has been made from the beginning of dark-field images for different reflections illuminating the entire grain in electron micrographs. The fact has been conveniently overlooked that the entire grain is never uniformly and identically illuminated from each imaging—in fact, there is always a sub-structure strongly suggesting the presence of nanometer-level micro-crystals with different orientations (Anantharaman 1988a).

(ii) Despite the early assertions that the X-ray diffraction patterns of icosahedral phases cannot be indexed to any Bravais lattice, cubic and orthorhombic unit cells have been proposed (Pauling 1987a,b,c; Anantharaman 1989) and satisfactory agreement between observed and calculated interplanar spacings also demonstrated for many icosahedral phases.

(iii) Many deviations from ideal quasicrystallography have been noted in electron diffraction patterns. The ten spots in any circle are generally identical neither in shape nor in intensity (Anantharaman 1988a) and many spots seem to be due to overlap of two or more reflections (Vecchio and Williams 1988). Measurement of angles between rows of reflections shows deviations from the expected 36° , while positions of diffraction maxima in any row of reflections show deviations from the expected Fibonacci sequence (Pauling 1989a,b).

(iv) The positions and shapes of some electron diffraction spots strongly suggest that they are formed by double diffraction (Pauling 1989a,b). In fact, a detailed comparison of Debye-Scherrer and electron-diffraction patterns of the equilibrium Al-Cu-Fe icosahedral phase has recently confirmed (Anantharaman 1994a) the role of double diffraction in the latter. This study has also established that the observed five-fold diffraction symmetry in such phases is due to the special geometry of their unit cells and the co-existence of five sets of micro-crystals with a special 72° orientation relationship between them in every grain or single crystal of these phases.

(v) More than one orientation has actually been observed in high-magnification electron micrographs of icosahedral phases. Ball and Lloyd (1985) reported on the appearance of all five orientations in the $\text{Al}_6\text{Li}_3\text{Cu}$ phase, while Rao and Anantharaman (1988) could detect three or four orientations 72° to each other in the Al-Cu-Mg phase through lattice resolution or Moiré fringes.

(vi) The non-icosahedral, micro-crystalline nature of the Al-Li-Cu quasicrystalline phase was also brought out effectively by Vecchio and Williams (1988) through convergent-beam electron diffraction (CBED) studies. Asymmetries observed in CBED patterns showed that the crystal symmetry is not truly five-fold. By careful thinning of the specimen to a wedge-like shape, the twinned micro-crystalline nature of the phase was brought out by these investigators in a striking fashion.

The most clinching evidence in favour of traditional crystallography and against quasicrystallography has just been put on record by a French team (Fettweis *et al* 1994) which has been quite enthusiastic about the quasicrystal concept until two

years ago. Analysing systematically their single crystal X-ray diffraction data from decagonal $\text{Al}_{63}\text{Cu}_{17.5}\text{Co}_{17.5}\text{Si}_{2}$, these researchers come to the following conclusion: 'High resolution experiments using synchrotron radiation are well interpreted within the scope of a micro-crystalline model. The decagonal needles are in a micro-crystalline state formed of crystalline domains having 72° orientation relations'.

In the light of the above findings, it is appropriate to examine in some detail the available two crystallographic models proposed and developed over the years by Pauling and the present author respectively for quasicrystals in general and icosahedral phases in particular.

4. The Pauling hypothesis

As is well recognized, Pauling and his collaborators used the stochastic method of trial-and-error with educated guesses (Pauling 1955) very frequently and highly successfully since the fifties of this century in the formulation of structure models for complex inter-metallic phases, particularly in aluminium alloys. Using the same method, Pauling studied X-ray and electron diffraction patterns of icosahedral phases obtained from other investigators and came out with many proposals of cubic unit cells that can lead to five-fold diffraction symmetry through icosatwinning. He proposed first a 1168-atom cubic unit cell with $a = 26.73 \text{ \AA}$ on the pattern of NaCd_2 (Pauling 1985) for Al-Mn icosahedral phase (*i*-Al-Mn). Realizing that the sequence of electron diffraction maxima in the five-fold patterns could not be satisfactorily explained with such a cubic cell on the basis of twinning, he modified his unit cell to one with 820 atoms and $a = 23.36 \text{ \AA}$ (Pauling 1987a,b,c), made up of eight 104-atom clusters, each being a complex of twenty Friauf polyhedra with icosahedral symmetry. According to this model, the eight 104-atom complexes adopt the β -W structure i.e. two complexes at 000 or $1/2 \ 1/2 \ 1/2$ positions and six complexes at $1/2 \pm 1/4 \ 0$, $\pm 1/4 \ 1/2 \ 0$ and $0 \ 1/2 \pm 1/4$ positions in the large unit cell, with twelve atoms lost in the process of sharing of pairs ($8 \times 104 - 12$). Incidentally, such clusters of 104 atoms are known to occur in $(\text{AlZn})_{49}\text{Mg}_{32}$ and other Frank-Kasper phases (Bergman *et al* 1957).

Following availability of reliable X-ray powder and electron diffraction patterns from equilibrium icosahedral phases like *i*-Al-Cu-Fe, Pauling examined their very many weak and very weak X-ray reflections, particularly at very low Bragg angles, 'which are ten times as numerous as the stronger peaks' (Pauling 1988a-d) as also the distribution of spots in two-fold axis electron diffraction patterns (Pauling 1989a,b) and came to the conclusion that much larger cubic unit cells were necessary to explain the available X-ray and the electron data. Thus he proposed a body-centred cubic cell with the cube edge value around $52 \text{ \AA}$ and containing over 9,900 atoms for *i*-Al-Cu-Fe and an even bigger face-centred cubic unit cell ($a = 66 \text{ \AA}$ with over 19,000 atoms!) for *i*-Al-Mn (Pauling 1989a,b). He invoked the β -W arrangement again for *i*-Al-Cu-Fe, but with very large complexes, each an icosahedral packing made up of no less than forty-five 104-atom clusters at 000 and $1/2 \ 1/2 \ 1/2$ positions, and individual 104-atom clusters in the other six positions.

Pauling based his work on experimental evidence from others and often could not (or did not) index all X-ray reflections on the basis of his unit cells. Nor did he explain why so many expected reflections were not observed. The agreement

between observation and calculation was not always satisfactory and the indices (*hkl*) of strong or medium reflections were sometimes far from convincing e.g. 13·85, 21·13·8, 34·21·13 in case of *i*-Al-Cu-Fe. Although a space group viz. No. 233, was assigned to this cubic unit cell, no effort was made to show matching of observed X-ray intensities with calculated values. In his own words (Pauling 1991) such structures are, 'of course, hypothetical at the present time' ... 'It is not possible at the present time to check this proposed structure and locate the atoms'.

However, Pauling was all along convinced that his proposals were heading to a 'unified structure theory' for thermodynamically stable as well as non-equilibrium metastable phases in aluminium alloys. By invoking cubic crystallites with structures closely similar to those of known intermetallic compounds for the new icosahedral phases, he strongly felt that his unified theory 'has the desirable feature of conforming to the known principles of structural chemistry'. One cannot do better than quote Pauling himself on his vision of a unified structure theory (Pauling 1988a-d):

'The formation of large icosahedral clusters is expected for an alloy of two or more metallic elements with different atomic radii, and these clusters, probably with a range of values of the number of atoms in the outer shell, can be expected to be present in the molten alloy. If the molten alloys were to be quenched extremely rapidly it would form a metallic glass, with the clusters having the same random orientation as in the melt and being piled together as in the melt. With somewhat less rapid quenching the clusters would begin to form crystallites. These crystallites might in some cases, as for Al_6CuLi_3 , have the thermodynamically stable structure. Usually, however, as for $(\text{AlZn})_{49}\text{Mg}_{32}$, the thermodynamically stable structure involves sharing the atoms in the outer shell between clusters, which requires time, so that instead the alloy crystallizes with a metastable structure that involves an easily assumed arrangement in which the clusters that were present in the liquid pile together in a crystallographically simple way, such as cubic close packing of the clusters, 4 clusters in a face-centred cube.

In fact, no such 4-cluster quasicrystals have been found; instead, the structures are based on the β -W arrangement, with the unit cube containing 8 clusters. The reason for the selection of β -W arrangement is obvious. It is that the Bergman-Waugh-Pauling triple-shell cluster of 104 to 136 atoms has icosahedral point group symmetry and accordingly strives to coordinate 12 other clusters about itself at the corners of the icosahedron

The diffraction maxima in these grains have intensities and positions determined by three structure factors: the structure factor of the cluster, the structure factor of the cubic crystallite and the structure factor representing the interaction of one crystallite with the other'.

5. The author's model

The present author has been studying carefully and systematically since 1987 X-ray powder and electron diffraction patterns from icosahedral and decagonal phases, some of them obtained from other investigators and some generated by him in

Indian laboratories (at Varanasi, Patiala and Delhi) or elsewhere during short visits (Tokyo in 1987, Oxford in 1989, Grenoble in 1990, Dortmund in 1993 and Dresden in 1994). He has thereby been trying to understand the atomic arrangements in these new and exotic phases in his capacity as a structural metallurgist operating within the framework of traditional crystallography. His objective has been not only to understand and explain the observed diffraction effects satisfactorily, but also to propose and develop a model that can account for all experimental observations related to the formation and transformation as also physical, chemical and mechanical properties, of these phases and relate them to other equilibrium as well as non-equilibrium phases in aluminium alloys. In view of the universal observation of icosahedra, icosahedral order or icosahedral motifs in practically all complex Al-TM alloy phases, the starting point for the author's model has been the icosahedral atomic cluster suggested by Frank (1952) and later expanded to include pentagonal atomic chains through vertex connection of icosahedra by Hume-Rothery and Anderson (1960). It is of some interest to record here that two of the earlier models put forward by quasicrystallographers themselves were based on icosahedra either joined randomly by their edges (Schechtman and Blech 1985) or connected through their vertices with bond-orientational order (Stephens and Goldman 1986).

As has been lucidly brought out by Shoemaker and Shoemaker (1988), chemical crystallographers have long been familiar with the variety of ways in which icosahedra can link together to propagate the icosahedral orientation through space. As shown in figure 1 two icosahedra can join or get welded through sharing a vertex (figure 1a), or an edge (figure 1b) or a face (figure 1c), with two types of orientations (A and B) emerging, the orientation B derived from orientation A by the operation of a mirror plane. The three modes of linking separated icosahedra are brought out in figure 2, through intervening tetrahedra (figure 2a), or octahedra (figure 2b) or squares made up of opposite edges (figure 2c). Needless to say, despite minor distortions in the joining process, the shapes and sizes of unit cells of the resulting crystal structures get determined and hence may be computed on the basis of the icosahedron's geometry, as modified by requirements of the concerned linkages.

The primary building block for icosahedral and decagonal phases, as also their many rational approximants, is identified in the author's model (Anantharaman

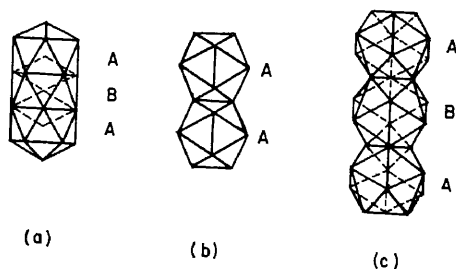


Figure 1. Modes of joining icosahedra: (a) two icosahedra (both having orientation A) sharing vertex to generate a third icosahedron in between with orientation B, (b) two icosahedra sharing an edge and (c) icosahedra sharing a face with orientations alternating.

1993, 1994) as the orthorhombic cell (figure 3) that can be visualized as forming through linkage in three perpendicular directions, with small expansion, contraction and/or distortion, as may be required, of icosahedral clusters containing more than one species of metallic atoms. Following atom-sharing in this joining process involving all three connections described above (figures 3a,b and c), this basic orthorhombic cell (actually a distorted icosahedron) ends up with 6 or 7 effective atoms in it, the latter number in case of filled icosahedra with 13 atoms, one of them in the body centre. This basic cell can be assigned the space group P_{mmm} (No. 47) and provided 16 possible atomic positions for the 6 or 7 effective atoms in it, with an unusual face-centred-cum-body-centred-cum-edge-centred symmetry that facilitates ordering of different atoms and vacancies in diverse ways in superstructures. In fact, this unit cell can be halved as shown in figure 4a, with 8 atomic positions for 3 to 3.5 effective atoms, the former characterized by two variants of face-centred cubic orthorhombic positions that enable maintenance of appropriate inter-atomic distances, partial occupancy of atomic sites and vacancies at required levels in superstructures.

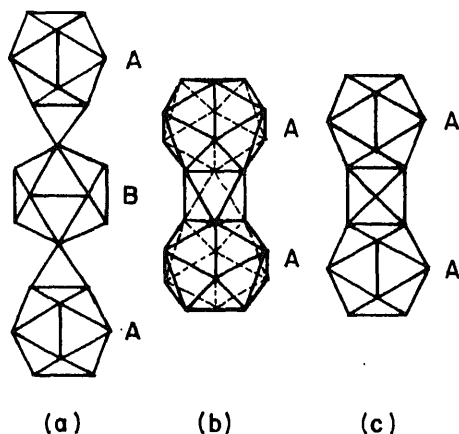


Figure 2. Modes of linking separate icosahedra: (a) icosahedra join, sharing opposite edges with tetrahedra that separate them, (b) icosahedra join, sharing opposite faces with octahedra that separate them and (c) icosahedra join, sharing opposite edges with octahedra that separate them.

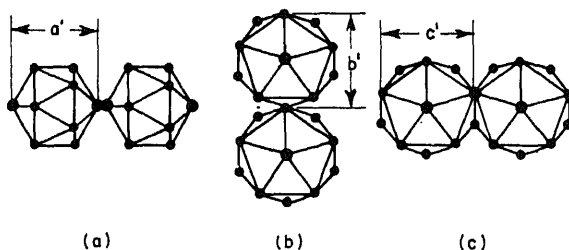


Figure 3. Emergence of the basic orthorhombic cell with parameters a' , b' and c' by the coming together or linking of icosahedra in all three directions with (a) vertex, (b) face and (c) edge connections respectively.

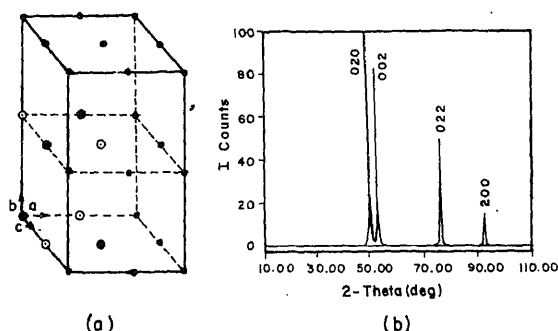


Figure 4. Refined basic orthorhombic cell, the building block for icosahedral phases, decagonal phases, and their rational approximants with (a) eight atomic positions, made up of two variants of four positions each and (b) computed powder diffraction intensities therefrom with equal partial occupancy by aluminium atoms only.

It has further been postulated by the author that the icosahedral, decagonal and rational approximant phases crystallize with large orthorhombic unit cells that are only superstructures of this small basic cell, built through complex ordering of dissimilar atoms and vacancies. If a' , b' and c' are the parameters of the basic cell with 3 to 3.5 effective atoms, ma' , nb' and oc' give the lattice parameters a , b and c respectively of the concerned orthorhombic cell, where m , n and o are integers. The values of these integers can generally be arrived at for a particular phase through careful analysis of its X-ray/neutron Debye-Scherrer patterns, particularly the positions of the few strong and medium reflections on the one hand and the many weak and very weak low-angle reflections on the other. In fact, as mentioned earlier, the weak reflections with the lowest Bragg angles offer important clues regarding the actual size of the unit cell. Incidentally, this family of orthorhombic crystals can also be indexed on a hexagonal or rhombohedral crystallographic framework, if so desired.

As explained earlier (Anantharaman 1989, 1990), the basic cell parameters a' , b' and c' can be arrived at, approximately to start with, from the geometry of the ideal icosahedron whose edge length is taken as the average interatomic distance computed for the concerned alloy composition. This approach has led (Anantharaman 1994) to determination of the following lattice parameter values in the Al-Mn system: (a) For the icosahedral phase (*i*-Al-Mn): $a = 6a' = 15.288 \text{ \AA}$; $b = 4b' = 17.376 \text{ \AA}$; $c = 4c' = 16.548 \text{ \AA}$, (b) for the decagonal phase (*d*-Al-Mn): $a = 6a' = 15.258 \text{ \AA}$; $b = 3b' = 12.552 \text{ \AA}$; $c = 4c' = 16.418 \text{ \AA}$ and (c) for some rational approximants of decagonal phases (including ternary alloys): $a = 3a'$; $b = 3b'$; $c = 6c'$ (here the actual values will vary according to the chemical composition).

For many icosahedral phases, as also decagonal phases which display polytypism along the b direction, excellent agreement between observed and calculated interplanar distances (d_{hkl}) has been demonstrated, with strong and medium reflections showing appropriate indices like 200, 020, 002, 022 etc of the basic cell (Anantharaman 1993, 1994). Figure 4b shows the computed X-ray intensity values for the first 32

powder reflections from the primitive basic cell (figure 4a) with only Al atoms in equal partial occupancy of the atomic sites. These data reflect a truly remarkable state of affairs, that has intrigued and confused crystallographers working in this field for many years. Thanks to the extraordinary symmetry and equal partial occupancy of the atomic sites, most reflections end up here with zero structure factor! It is most gratifying to note that only four X-ray reflections viz. 020, 002, 022, and 200 in that order, make their appearance in the Bragg-angle range under consideration, the first two being the very strong reflections appearing close to each other and with an overlap in all icosahedral and decagonal phases respectively.

This model also explains many other features associated with these new phases. The nucleation problem gets solved, the growth of these phases starting homogeneously from icosahedral atomic clusters already existing in the alloy melts. The close relationship between icosahedral and decagonal phases is highlighted by the dimensions of their unit cells. In case of *i*-Al-Mn, despite the inevitable distortion due to linking of icosahedral clusters, the *b/c* ratio remains at 1.05, as in the ideal icosahedron. However, there seems to be more interpenetration and greater distortion of the icosahedron in the formation of *d*-Al-Mn. All the same, the observed epitaxial growth of *d*-Al-Mn on *i*-Al-Mn can be understood on the basis of their very close *a* and *c* parameters. A single space group viz. No. 47, has been assigned for the first time to all these phases. The extra atomic sites in the unit cells allow for maintenance of appropriate inter-atomic distances and the occurrence of a range in chemical composition. The five-fold diffraction symmetry gets explained in this icosahedral model through random changes in direction by 72° during crystal growth and unusual orientation relationships (Bendersky *et al* 1989). Properties like hardness, brittleness, electrical resistivity etc of these phases can now be understood as due to each grain or crystal being a complex mosaic or irregularly-shaped and considerably inter-twined microcrystallites. A single crystal thus becomes a myth as far as these phases are concerned.

As an example, the X-ray data obtained recently by the author at Dresden, Germany, on a rapidly solidified and annealed *i*-Al-Cu-Fe phase in a Siemens Rotating Anode X-ray Diffractometer are presented in table 2 in nanometer units. The agreement between calculation and observation is extremely good for all reflections, which were invariably sharp, except perhaps for the first weak reflection at a rather low Bragg angle, where the location of any peak is subject to uncertainties caused by the nature, size and shape of the specimen, its mounting pattern and related instrumental factors. It is noteworthy that all recorded reflections have indices (*hkl* values) common to both face-centred and body-centred cubic structures, as in case of the basic cell (figure 4b). As can be appreciated, once the extraordinary symmetry of the basic cell gets broken through complex ordering of dissimilar atoms and vacancies, all X-ray reflections start appearing, albeit very weak in most cases, as from primitive orthorhombic structures.

The only problem yet to be sorted out concerns satisfactory matching of calculated and observed X-ray/neutron intensities from *i*-Al-Cu-Fe and similar equilibrium icosahedral phases. As any crystallographer will readily concede, it is quite a challenge to place correctly so many atoms (around 288) belonging to three elements (Al, Cu and Fe in this case) in an ordered fashion with partial occupancy and vacant sites in a large superstructure (made up of 96 basic cells and with 576 possible atomic sites). However, it is only a matter of time, effort and appropriate computer software for this problem also to be solved satisfactorily.

Table 2. Comparison of calculated and observed interplanar distances (d_{cal} and d_{obs} in nanometers) and observed relative intensities (I_{obs}) for Debye-Scherrer reflections from Al-Cu-Fe icosahedral phase.

No.	<i>hkl</i>	d_{cal}	d_{obs}	I_{obs}	No.	<i>hkl</i>	d_{cal}	d_{obs}	I_{obs}
1	020	0.842	0.833		17	624	0.204	0.204	2
2	220	0.557/			18	008	0.200	0.200	100
3	202	0.545	0.551	3	19	644	0.189	0.188	1
4	040	0.421/			20	428	0.173	0.173	3
5	004	0.401	0.415	3	21	448	0.163	0.162	2
6	042	0.373	0.374	13	22	088	0.145	0.145	13
7	420	0.340/			23	0.10.6	0.143	0.142	4
8	402	0.337	0.339	15	24	10.44	0.132	0.133	1
9	224	0.325	0.324	12	25	22.12	0.130/		
10	440	0.279	0.280	3	26	848	0.130	0.130	1
11	600	0.248	0.245	7	27	12.00	0.124	0.124	36
12	602	0.237	0.238	3	28	12.42	0.118	0.117	2
13	444	0.229	0.229	2	29	12.80	0.107	0.107	20
14	604	0.211/			30	12.08	0.105/		
15	080	0.211	0.211	94	31	0.16.0	0.105	0.105	15
16	642	0.206	0.206	2	32	00.16	0.100	0.100	1

Unit cell: Orthorhombic	$a = 1.4868 \text{ nm}$
Space group: P_{mmm} (No. 47)	$b = 1.6840 \text{ nm}$
I_{obs} : rounded to integers	$c = 1.6024 \text{ nm}$
(Weak reflections with I_{obs} less than 1.0 are not recorded).	

6. The unified crystallographic approach

Starting with icosahedral atomic clusters in alloy melts, that are made up of atoms of dissimilar sizes like those of aluminium and the transition metals, it is now possible to survey the whole field of complex phases in aluminium alloys and look for the inter-connections between the three major groups viz. (a) glassy or amorphous phases, (b) phases built with the orthorhombic basic cell, as described by the author, and (c) phases built with icosahedral clusters of different sizes, as visualized by Pauling.

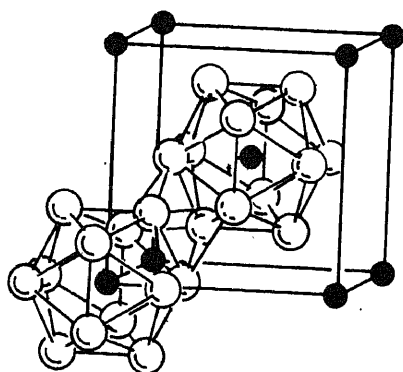
The alloy melts may be expected to contain individual icosahedra made up of 13 or 12 atoms, separated from one another at higher temperatures. On cooling, these icosahedra may join together through their vertices to produce pentagonal atomic chains with ordering, that can stabilize the alloy melt. Such stabilization may lead to deep eutectics in the concerned alloy systems at compositions like Al_{12}T , Al_{11}T , Al_{11}T_2 , Al_{10}T_2 , Al_{10}T_3 , Al_9T_3 , Al_9T_4 and Al_8T_4 for binary alloys made up of aluminium and one transition metal (T). The stabilization of the molten alloy may be easier for ternary and more complex alloys because of smaller atoms with different atomic radii becoming available for the ordering process. Rapid solidification of such alloys may lead to the formation of metallic glasses made up of individual icosahedra with random orientation and of broken, distorted and/or intertwined pentagonal chains, particularly in ternary and more complex aluminium alloys.

With decrease in cooling velocity, the icosahedral clusters and/or pentagonal chains in the melt may come together in all three directions to build up icosahedral, decagonal and the so-called rational approximant phases, as visualized by the author.

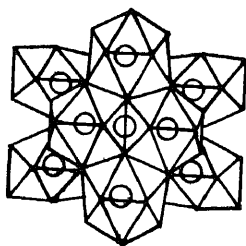
Chemical composition, nature and number of alloying elements and actual cooling velocity – all will play a role in deciding the concerned orthorhombic structure (that can be viewed as hexagonal or rhombohedral as well) for these phases. Less imperfect and more stable phases seem to need higher transition metal content and two or more alloying elements as in case of *i*-Al-Cu-Fe, *i*-Al-Cu-Ru and *d*-Al-Cu-Co. The decagonal phases may display different stacking sequences in one direction i.e. show polytypism, with stacking faults in some cases. It is attractive to consider all these as forming a special group of ‘Hume-Rothery phases’, even though the criteria are yet to be clearly understood and satisfactorily worked out for such an eventuality.

With normal cooling, individual and separate icosahedra may build up cubic, especially body-centred cubic (bcc) structures. Taking, as the first example, Al_{12}W , Al_{12}Mo , Al_{12}Cr , Al_{12}Mn , Al_{12}Re , etc with two 13-atom clusters, the cluster at the origin gets linked to the cluster at the body centre by an octahedron, sharing opposite faces with both (figure 5a). Accordingly, the sequence along the body diagonal in this bcc structure is A, A, A ... (see figure 2b). Bigger icosahedral clusters may also form, starting from the 13- or 12-atom icosahedra, and in fact, have been identified according to their sizes as Mackay icosahedra, ‘soccer ball’ etc. These also lead to bcc structures, the best known among them being the Frank-Kasper or T-phases containing 162 atoms. It was shown by Cenizal *et al* (1985) that the T-phase clusters can also be described in terms of linking or packing of icosahedra (see figure 5b). In this approach a shell of 12 centred icosahedra is created through edge-sharing, with the 12 inner vertices of these icosahedra forming an inner icosahedron with its central atom missing. The 13 icosahedra all have the same spatial orientation. The central icosahedron has to be somewhat smaller than the outer ones, just as the central atom has to be smaller than the ones forming the central icosahedron. This latter circumstance may well be the reason for the suspected absence of the central atom in T-phase structures, as also in $\alpha\text{-(Al, Si)}_{57}\text{Mn}_{12}$ and related phases (see Guyot and Audier 1985). In all such bcc structures, in principle, it should be possible to arrive at the lattice parameters approximately, as in the author’s model for icosahedral and decagonal phases, from the geometry of the inner icosahedron and the outer shells. In fact, the actual nature of the linkage between icosahedra may well be settled through such geometrical considerations.

To sum up, the golden thread running through the numerous Al-TM complex phases viz. metallic glasses, icosahedral phases, decagonal phases, rational crystalline approximants, Frank-Kasper and other equilibrium phases, can now be identified as the icosahedral atomic cluster present in all Al-TM alloy melts. Starting from such clusters, the crystalline phases form through homogeneous nucleation from them in two ways, one leading to orthorhombic, hexagonal and rhombohedral structures and the other to cubic structures, while the metallic glasses form by the freezing-in of individual clusters and vertex-joined pentagonal chains of atoms from the liquid state. The chemical composition of the alloy, as also the relative sizes and electronic structures of the different atoms in it, decide the mode of solidification under equilibrium conditions i.e. slow cooling from the melt. On the other hand, the high rates of cooling in rapid solidification may modify and change this mode drastically to produce different non-equilibrium phases with unusual 72° orientation relationships and complex interfaces between the microcrystallites that generally



(a)



(b)

Figure 5. (a) Unit cell of $\text{Al}_{12}M$ (when $M = \text{W, Mo, Cr, Re or Tc}$) with 13-atom clusters at origin and body centre linked by an octahedron sharing opposite faces, (b) cluster of 12 icosahedra sharing edges to define a larger icosahedron in Frank-Kasper or T-phases. One may note the distortions necessitated by the close approaches of atoms in icosahedra that are joined by edge-sharing.

constitute every grain in such polycrystalline materials. Needless to say, further accurate experimentation, painstaking analysis of available data and sophisticated computational procedures will all be needed to confirm this unified crystallographic approach.

In the author's view, Pauling grasped intuitively, rather than through a logical and cogent thinking process, the structural unity underlying complex crystalline and so-called quasicrystalline phases in aluminium alloys. He could not possibly put it across effectively, even though he authored many papers, as he worked practically alone in this area, depended heavily on the experimental data of others and also faced considerable hostility from the highly vocal and hyperactive leaders on the quasicrystallography bandwagon. His anger and anguish at the early turn of events led to some strong pronouncements e.g. 'this nonsense about quasicrystals' and 'I have difficulty getting my papers on the subject published' (Pauling 1986). He was seemingly on the right track, however, and his assertion in an interview that 'history is on my side' (Pauling 1993) may well prove to be prophetic.

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Development of ultra light magnesium–lithium alloys

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Abstract. Magnesium–lithium alloys are among the lowest density metallic materials. Addition of lithium, with a relative density of 0.53, in magnesium reduces the density of the alloy significantly. Furthermore, addition of nearly 11 wt.% lithium converts hexagonal close packed structure of pure magnesium to a body centered cubic lattice, markedly improving formability of the alloy. The development of these alloys, however, had been hampered due to the high reactivity of lithium and magnesium in the molten state and also, due to poor creep resistance and instability of mechanical properties at room temperature. In an attempt to indigenize these ultra light alloys for possible applications in Indian satellite programme, detailed research work was initiated in DMRL. The difficulties associated with producing sound cast ingots have been overcome by controlling melting and casting parameters of these alloys. Extensive work has been done on structure–property correlation of alloys with varying lithium content and minor alloying additions. Based on these work, advanced magnesium–lithium alloys have been developed with improved tensile properties, room temperature stability and creep resistance. Wrought products (plates/sheets) of magnesium–lithium alloy have been supplied to ISAC, Bangalore and are being used in their INSAT-2 programme. This paper describes the systematic studies carried out in the laboratory to indigenize these ultra light alloys.

Keywords. Ultra light Mg–Li alloy; flux cover melting; ingot casting; instability; mechanical properties; creep resistance; microstructure.

1. Introduction

Low density of magnesium (1.74 g/cc) has led to its association with transportation and especially, with aerospace industry which has provided great stimulus to the development of magnesium-based alloys during last few decades. In the course of the past work, various alloying elements have been added to magnesium so as to produce alloys of high strength, high creep resistance and low density. The development of magnesium–lithium alloys began in the early 1930s. The object of this early work was the development of light weight magnesium–lithium alloys exhibiting higher strengths, better formability and less directionality of properties than conventional magnesium alloys. Lithium, with a relative density of 0.53, is the lightest of all metals and has extensive solid solubility in magnesium (Nayeb-Hashemi *et al* 1984). Furthermore, addition of nearly 11 wt.% lithium converts hexagonal close packed structure of pure magnesium to a body centered cubic lattice, markedly improving formability of the alloy (Munroe 1966).

In view of the aforementioned characteristics, a number of attempts have been made to develop Mg-based alloys with lithium as major alloying additions. However, these attempts met with difficulties associated with melting and casting (Jackson *et al* 1949; Saia and Edelman 1962; Saia *et al* 1967; Saia and Edelman 1968; Beniere *et al* 1968), instability of mechanical properties at room temperature (Jones and Hogg 1957; Raynor 1959; McDonald 1968, 1969; Alamo and Banchik 1980;

Kalimullin and Berdnikov 1986; Das and Fraser 1989) and excessive creep at relatively low stresses (Raynor 1959; Jackson and Frost 1967). Despite considerable effort in Europe and USA it appeared that the only practical possibilities were to produce strong magnesium–lithium alloys which were not stable or stable magnesium–lithium alloys which were not strong and subsequently this development work was abandoned (Frost 1965). Further, the incomplete understanding of the strengthening mechanism of this alloy system led to the failure of developing this alloy into a potential material for aerospace industries.

1.1 *Development efforts at DMRL*

In the recent past, the demand for magnesium–lithium alloy components has considerably increased for use in aerospace and allied fields where reduction in the intrinsic weight of the design is of paramount importance. Consequently, magnesium–lithium alloys have been investigated more intensively in the last decade mainly to overcome their limitations as potential materials for various structural applications. In the mid 80s, a research programme was initiated at the Defence Metallurgical Research Laboratory (DMRL), Hyderabad for the indigenous development of magnesium–lithium alloys via ingot metallurgy route in order to meet the requirements of the Indian space industry. It is the purpose of the present paper to describe the systematic studies carried out at various stages of continuing magnesium–lithium development programme in the laboratory. Current applications of these alloys, together with the recent developments on this alloy type are also discussed within the context of the present paper.

2. **Melting, casting and characterization**

In the present study, magnesium and lithium were used as pure metals, while aluminium and other alloying elements were added in the form of master alloys. These materials were added with the intention of investigating the viability of producing magnesium–lithium alloys from commercially available raw materials. It may be mentioned here that the past work on these alloys were mostly carried out using ultra pure materials. The impurity contents of raw materials and flux covers used in the present study are given in table 1. Chemical compositions of different alloys prepared under halide flux covers using commercially available raw materials are given in table 2. Details of the melting, casting and fabrication techniques have been reported previously (Singh and Chakravorty 1988a, b; Singh *et al* 1989a). Briefly, Mg–Li–Al alloys were made by mixing molten magnesium and aluminium–magnesium master alloy in a mild steel crucible at around 1023 K and pouring over molten lithium, separately melted in a stainless steel crucible and kept at around 573 K. The melt was then chill-cast in a mild steel mould. For the alloy with zirconium, magnesium and magnesium–zirconium master alloy were heated to a temperature exceeding 1073 K and then molten aluminium–magnesium master alloy was added to this melt just before pouring over molten lithium. Here special care was taken to minimize the operation time after aluminium addition. This was necessary to retain zirconium in the alloy. At this time, the kinetics of aluminium–

zirconium compound formation and also the extent of compound formation in the melt or subsequent to the casting is not clear. Nevertheless, chemical analysis indicated similar concentration of zirconium in various parts of the cast ingot. The cast ingots were rolled at 573 K. Rolled plates/sheets were solution-treated at 573 K for 1 h followed by ageing at 453 K for 2 h. Specimens for optical metallography were etched in 2% nital, whilst those for transmission electron microscopy were chemically polished in a solution containing 2% nitric acid in ethyl alcohol cooled below 283 K (Urakami *et al* 1970).

Tensile tests were performed in an INSTRON machine at various strain rates (from 4.4×10^{-5} to $1.8 \times 10^{-3} \text{ sec}^{-1}$) and temperatures (298 to 473 K). For elevated temperature tests, samples were soaked at testing temperature for 30 min. Tests were conducted in both longitudinal and transverse directions with respect to the rolling direction. For hot rolled plates, with thickness of more than 10 mm, round tensile specimens with gauge diameter of 6.35 mm and gauge length of 19 mm were used, while for thinner plates/sheets, flat tensile samples of 19 mm gauge length, 5 mm width and thicknesses less than 4 mm were used. Creep tests were performed on constant load machines with a lever ratio of 1:10 and extensions were measured with two parallel LVDTs. The static elastic modulus was measured by non-destructive resonance technique. Densities were measured using the two-fluid method, with air and ethanol as fluids. Scanning and transmission electron microscopy was carried out on ISI 100A and Philips EM430T microscope respectively.

3. Major achievements

3.1 Melting characteristics

A comparison of alloy compositions given in table 2 with impurity contents present in the raw materials and flux covers (table 1) indicates minor pick up of iron, nickel and calcium by the alloys during melting. The analysis, however, indicates relatively lower levels of sodium and potassium in the alloy. Lower levels of Na and K in the alloy are due to elimination of these alkali metals from the melt as vapours at holding temperatures (Singh 1994a). It has been observed that the presence of impurities other than sodium can be tolerated in the alloy to considerably higher levels (Jackson and Frost 1967). Therefore, minor pick up of iron, nickel and calcium observed during melting will not adversely affect the properties of alloy. These findings indicate that the melting process employing suitable flux covers and crucible materials appears to be a viable technology.

Table 1. Impurity contents (wt.%) of raw materials used in preparing magnesium–lithium alloys.

Metal/flux	Fe	Si	Na	K	Ca	Ni	Mn	SO ₄	Purity
Magnesium	0.008	<0.01	-	-	-	0.003	0.003	-	99.8
Aluminium	0.07	0.06	0.001	-	-	-	-	-	99.8
Lithium	0.015	-	0.005	0.004	0.006	-	-	-	99.8
LiCl	0.001	-	0.006	0.01	0.01	-	-	0.01	99.0
LiF	0.004	0.01	-	-	-	-	-	0.02	99.0

Non-reactivity of molten lithium with 304L stainless steel up to 873 K (Averill *et al* 1981) and very low solid solubility of iron in the molten magnesium (Polmear 1989) avoids possibility of metal–crucible reaction during melting. However, prior to pouring, alloys were held in 304L stainless steel crucible at temperatures well above 950 K. At this temperature, iron and nickel pick up in the alloy were observed due to corrosive attack of molten metal on crucible material. The dissolution of nickel in molten magnesium is a well observed phenomenon (Brace and Allen 1957). The dissolution of iron in the alloy, on the other hand, is not well understood. Considering low solubility of iron in magnesium in the present working temperature range, it may be stated that the corrosive attack of lithium controls the iron pick up in the alloy during holding period. Lithium, which does not attack 304L stainless steel up to 873 K (Averill *et al* 1981), perhaps becomes corrosive at higher temperatures. It has been reported that delay time prior to grain boundary penetration in 304L stainless steel by liquid lithium had a temperature dependence (Patterson *et al* 1975). The complexity of liquid lithium corrosion is also related to various other factors, such as thermal and chemical potential gradients, variations of elemental solubility as a function of temperature, role of interstitial contaminants in liquid lithium etc. The actual mechanism of attack on 304L stainless steel by magnesium–lithium alloy melt for iron pick up, however, needs further investigation.

To study the suitability of flux covers, the feasibility of various direct displacement reactions between molten metal and compounds present in the flux cover were worked out. Possible reactions of lithium with MgCl_2 and CaF_2 , present in magnesium flux, indicates reasonably higher limiting activity of reaction products (Singh 1994a). Thus use of magnesium flux cover over molten magnesium–lithium alloy will result in lithium loss as well as calcium pick up by the alloy ($\text{LiCl} + \text{LiF}$) flux, on the other hand, remains inert to the alloy system. Therefore, it can be safely used as flux cover for the alloy during holding period. However, minor pick up of calcium is observed in the alloy even when LiCl – LiF flux cover is used during holding period (table 2). This can be attributed to relatively higher level of calcium present as impurity in lithium chloride (table 1). Also, the inability of LiCl – LiF flux to cover molten magnesium–lithium alloy effectively results in loss of lithium as dross during holding period. Therefore, to minimize the loss of lithium during holding period, sulphur powder was sprinkled over the molten alloy which creates neutral atmosphere and minimizes atmospheric oxidation of the alloy to a large extent.

Table 2. Chemical compositions (wt.%) of different batches of magnesium–lithium alloys.

Charge composition (wt.%)	Melt size (kg)	Composition (wt.%) of the alloy								
		Li	Al	Zr	Fe	Si	Ni	Na	K	Ca
Mg–12Li–1.5Al	2	10.8	1.56	-	0.013	<0.01	0.005	<0.002	<0.002	0.008
	10	11.2	1.54	-	0.013	<0.01	0.005	<0.002	<0.002	0.006
	20	11.4	1.52	-	0.013	<0.01	0.004	<0.002	<0.002	0.006
	30	11.5	1.52	-	0.013	<0.01	0.004	<0.002	<0.002	0.005
	40	11.6	1.51	-	0.010	<0.01	0.003	<0.002	<0.002	0.003
	50	11.6	1.50	-	0.010	<0.01	0.003	<0.002	<0.002	0.003
Mg–15Li–1.5Al	10	13.8	1.55	-	0.014	<0.01	0.005	<0.002	<0.002	0.007
Mg–9Li–1.5Al	10	8.4	1.53	-	0.013	<0.01	0.005	<0.002	<0.002	0.006
Mg–4Li–1.5Al	10	3.8	1.52	-	0.011	<0.01	0.005	<0.002	<0.002	0.005
Mg–12Li–1.5Al–0.6Zr	10	11.4	1.57	0.14	0.013	<0.01	0.005	<0.002	<0.002	0.006

These observations point out the difficulties encountered in melting of magnesium–lithium alloys under halide flux cover. To avoid these problems, the alloy prepared under a flux cover must not be held in crucibles prior to pouring for unnecessarily long period not only to avoid loss of costly lithium but also to keep the iron, nickel and calcium contents of the alloy sufficiently low for better properties. Perhaps this technology can be improved further by replacing 304L stainless steel with suitable ceramic material as crucible material. However, for all other parts of the present work, magnesium–lithium alloys were prepared using 304L stainless steel and restricting the holding time to bare minimum (< 5 min).

3.2 Mechanical behaviour

Magnesium–lithium alloys can be classified into three major categories based on the constitutional phases present in the system (figure 1). They are: α alloys with lithium less than 5 wt.%, β alloys with lithium more than 11 wt.% and $(\alpha + \beta)$ alloys with lithium ranging from 5 to 11 wt.%. Different proportions of α and β in the alloy significantly changes the mechanical behaviour of this system. Mg–Li–Al alloys corresponding to each of these categories have been studied. Typical microstructures of α , $(\alpha + \beta)$ and β alloys are shown in figure 2. A

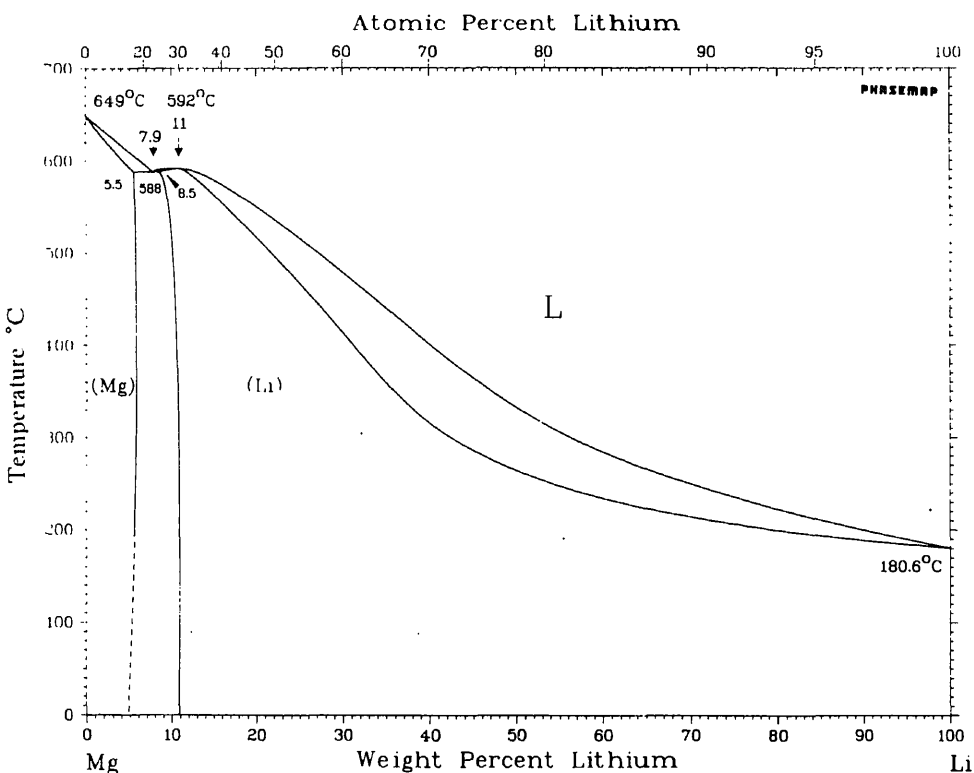


Figure 1. Equilibrium phase diagram of binary magnesium–lithium system.

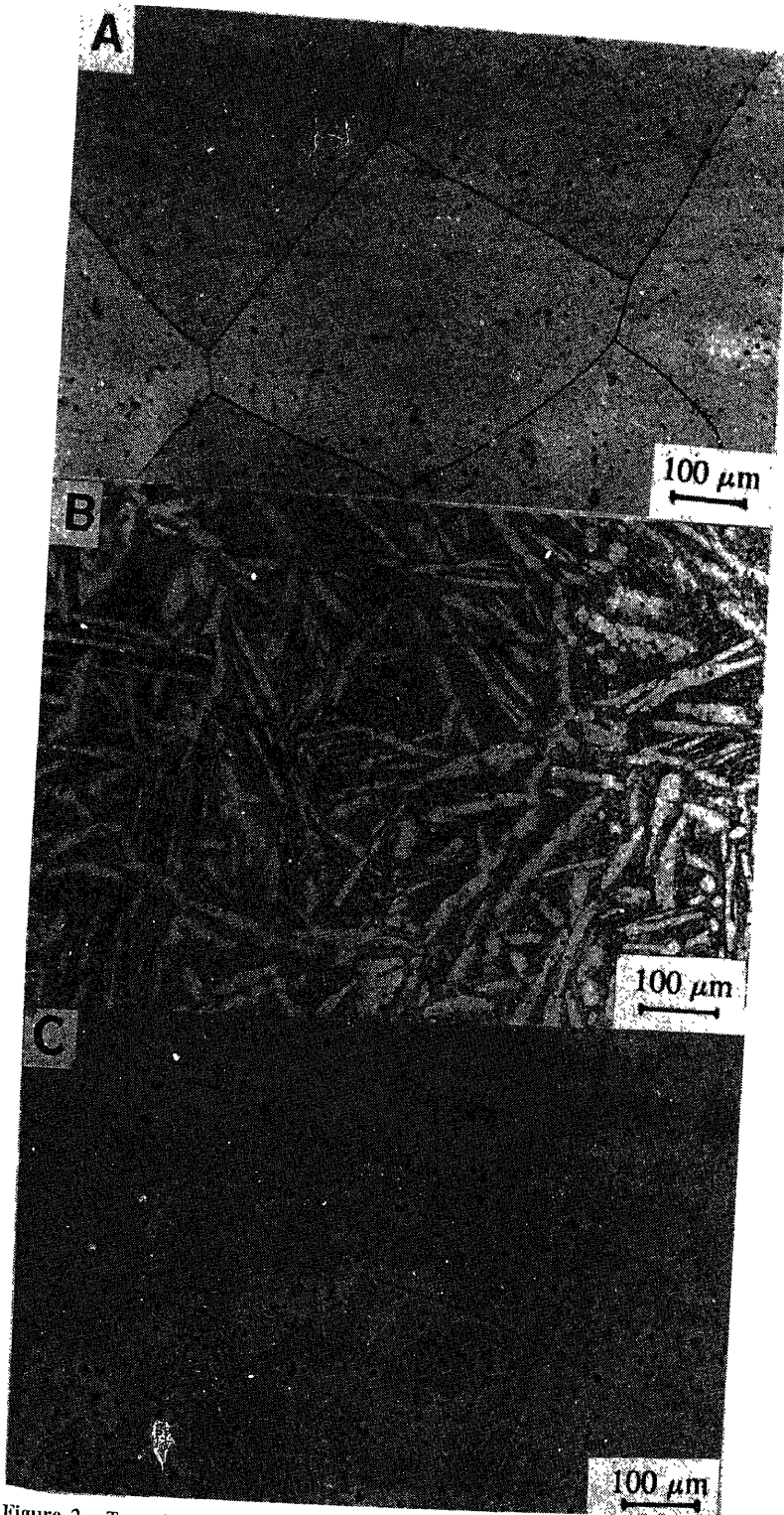


Figure 2. Typical microstructures of (A) α , (B) $\alpha + \beta$ and (C) β alloys.

comparison of different alloys based on ternary Mg–Li–Al system indicated that optimum balance of ductility, strength and stability is achieved in the alloy with around 11 wt.% lithium (Singh 1994a). Mg–11Li–1.5Al alloy was, therefore, selected as the base alloy for further studies.

2a Instability of mechanical properties: The instability of mechanical properties associated magnesium–lithium alloys has been reported by several workers (Jones and Hogg 1957; McDonald 1968; Singh and Chakravorty 1988a, c). Instability in these alloys is associated with very high atomic mobility of lithium, even at relatively low temperatures (Iwadata *et al* 1987). Exceptionally high vacancy concentration and the lithium atom jump frequency result, not only in great mobility for both vacancies and lithium atoms, but also in rapid transport of other solute species. This leads to rapid coarsening of precipitates in combination with rapid dislocation climb, which destroys the efficiency of conventional hardening mechanism. Magnesium–lithium alloys with different minor additions (Zr, Mn, Ce, Be, Y, Th and Nd) were cast, processed and heat treated under identical conditions to compare the effect of these elements on stability of mechanical properties of the alloy at room temperature. Tensile properties of all the alloys were evaluated in both rolled and stabilized conditions and are listed in table 3. It can be seen from this table that all the alloys studied show degradation in strength as a result of stabilization treatment. In Mg–Li–Al–Zr alloy, however, only a minor drop of around 6% in strength was observed after stabilization. The instability associated with this alloy, therefore, can be regarded as insignificant. Further, zirconium appears to be the most beneficial addition in improving the specific strength of the alloy at room temperature (Singh *et al* 1989b; Singh and Mishra 1990) as well as at elevated temperatures (Singh 1994a). This gives an indication that the Al_3Zr precipitates which have formed as a result of zirconium addition are much more stable than the precipitates normally present in the ternary Mg–Li–Al system. This is to be expected, since zirconium has lower diffusivity (Vesey and Bray 1963–64) and limited solid solubility (Emley and Duncumb 1961–62) in magnesium—the factors which govern particle coarsening kinetics (Wagner 1961). Limited transmission electron microscopy showed fine Al_3Zr precipitates at grain boundaries and also within the grains in Mg–Li–Al–Zr alloy (figure 3).

Table 3. Drop in strength as a result of stabilization treatment in magnesium–lithium alloys.

Alloy	Density (g/cc)	Tensile properties						Drop in strength (%)
		As rolled			Stabilized			
		0.2% PS (MPa)	UTS (MPa)	Elong. (%)	0.2% PS (MPa)	UTS (MPa)	Elong. (%)	
Mg-11Li-1.5Al	1.41	145	174	39	113	130	50	25
Mg-11Li-1.5Al-0.14Zr	1.45	170	220	25	140	207	17	6
Mg-11Li-1.5Al-0.35Mn	1.52	150	200	30	130	170	20	15
Mg-11Li-1.5Al-1.0Ce	1.60	150	205	25	120	170	12	17
Mg-11Li-1.5Al-0.013Be	1.41	165	180	35	110	135	40	25
Mg-11Li-1.5Al-0.2Y	1.47	150	185	30	115	160	25	14
Mg-11Li-1.5Al-0.1Th	1.50	160	185	25	120	160	30	14
Mg-11Li-1.5Al-0.47Nd	1.55	180	200	12	135	160	20	20

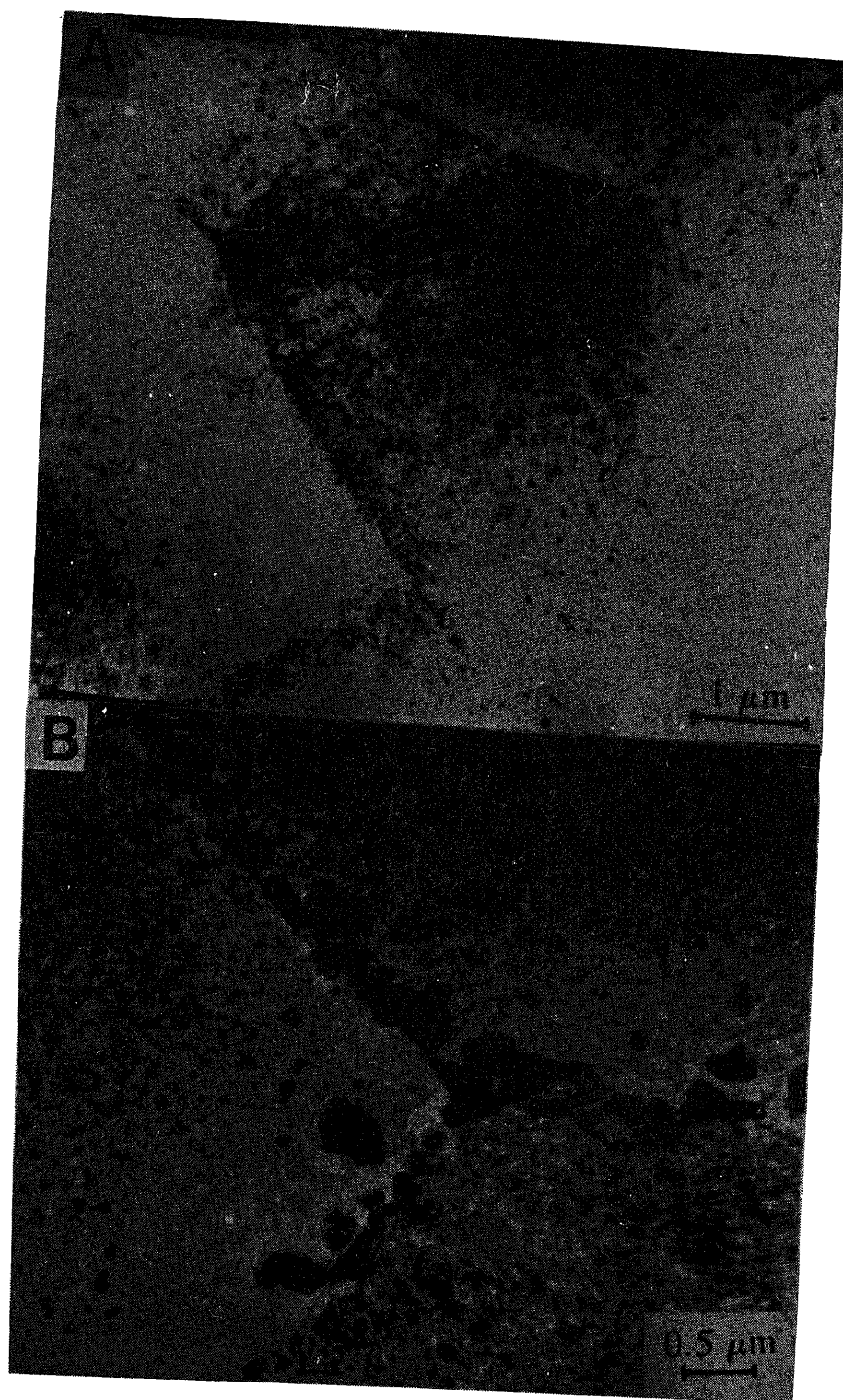


Figure 3. TEM micrographs of (A) Mg-Li-Al and (B) Mg-Li-Al-Zr alloys.

3.2b Ductility trough at elevated temperatures: Studies on temperature dependence of ductility in these alloys were also carried out. The tensile ductility of the Mg–Li–Al and Mg–Li–Al–Zr alloys at various temperatures in the range 233–473 K is shown in figure 4. It may be seen that the ductility of the Mg–Li–Al alloy drops significantly in the range 373–423 K. The ductility trend observed has been correlated with fractography (Singh 1994a). It is observed that below 373 K, these alloys are ductile with associated transgranular path (figure 5a). However, at higher temperatures (373–423 K), ductility decreases and a transition from transgranular to intergranular fracture is observed (figure 5b). This transition appears to be a result of localized diffusion of sodium and other alkali metals toward grain boundaries at elevated temperatures (Gur'ev *et al* 1980). Above 423 K, however, there is again a sharp recovery in tensile ductility due to dynamic recrystallization, which results in desegregation of alkali metals at grain boundaries (Singh 1994a). Also, dynamic recrystallization results in accommodation of stress concentration formed at prior grain boundaries. In presence of zirconium a significant change in this behaviour is observed. Zirconium, which improves tensile strength of the alloy by fine precipitation of Al_3Zr , has also been found to promote early recrystallization in the material (Singh 1994a, b). Thus the ductility trough, which is postulated to be accomplished by the competition of the two diffusion controlled processes i.e. the grain boundary cavitation and dynamic recrystallization, is minimized to a large extent in presence of zirconium.

3.2c Improvement in creep resistance: Figure 6 shows variation of steady state creep rate of Mg–Li–Al and Mg–Li–Al–Zr alloy with applied stress at room temperature. A comparison of the steady state creep rate data of these alloys clearly indicates remarkable improvement in creep resistance of the alloy after zirconium addition. It is important to note that Mg–Li–Al alloy creeps at a stress of 67 MPa, which is much below its yield strength of 113 MPa. On the other hand, the modified

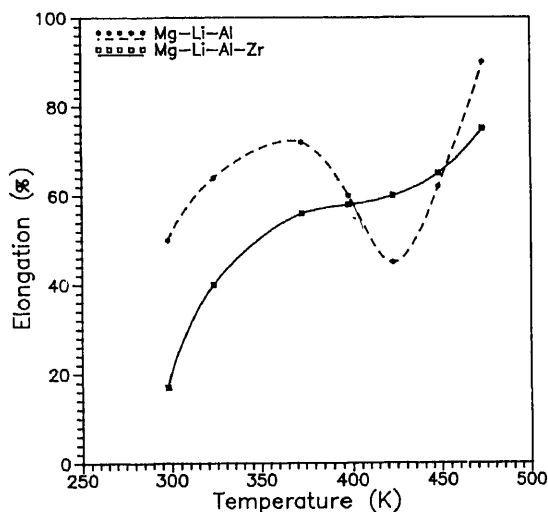


Figure 4. Effect of zirconium on high temperature ductility of magnesium–lithium alloy.

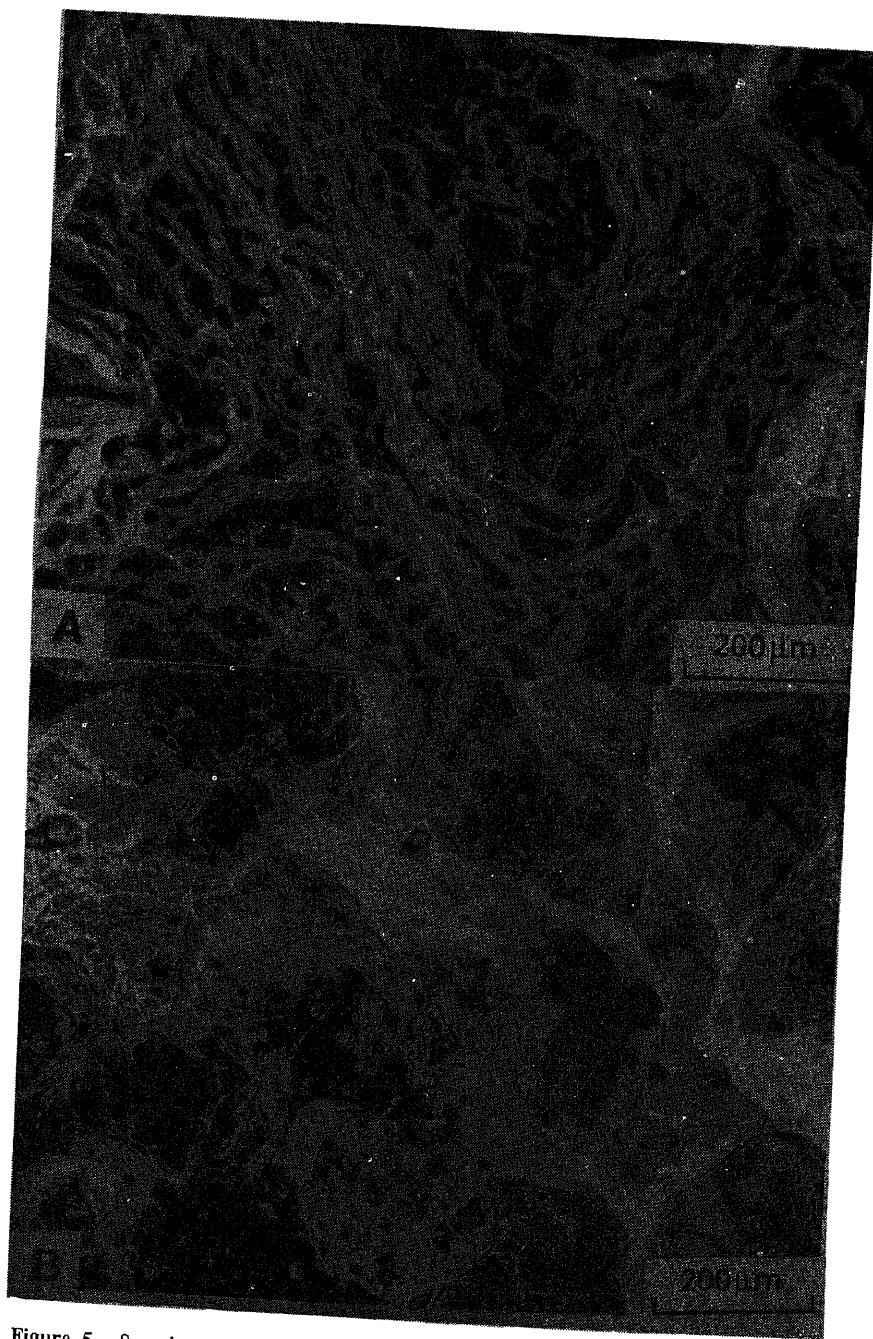


Figure 5. Scanning electron fractographs showing (A) transgranular and (B) intergranular fracture in Mg-11Li-1.5Al alloy.

Mg-Li-Al-Zr alloy does not creep at any measurable rate up to 130 MPa. This value is far closer to the yield strength (140 MPa) of this alloy at room temperature. The observed improvement has been correlated with delayed power law breakdown in the alloy containing zirconium (Singh 1994a).

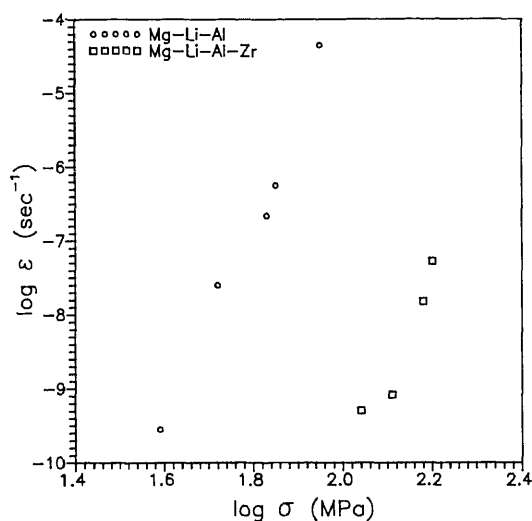


Figure 6. Variation of steady state creep rate with stress at room temperature.

2d Protective coatings: Magnesium–lithium alloys are well known for their poor corrosion resistance. The poor oxidation/corrosion resistance of magnesium–lithium alloys is related to their high chemical reactivity and to the segregation of alloying elements leading to localized cathodic centres. Initial oxidation rates are relatively low due to the formation of protective hydroxide film on the surface. After sometime, however, this protective film breaks down giving rise to higher rate of oxidation. Electrodeposition on these alloys are difficult due to their high reactivity in aqueous solutions. Extensive development work carried out at ISAC, Bangalore has culminated in the development of thermally stable coating (Sharma 1988). These coatings have been used successfully on magnesium–lithium alloy components by ISAC, Bangalore for use in INSAT-2.

Work in progress and future plans

As discussed above, minor additions of zirconium improves the tensile strength and creep resistance of Mg–Li–Al alloy significantly. In an attempt to further improve both the strength and the modulus of the alloy, work has been initiated to develop magnesium–lithium matrix composites. It has been reported that ceramic fibres/particles undergo significant degradation when kept in contact with molten lithium for a considerably longer duration (Mason *et al* 1989). Any reaction between reinforcement and matrix would lead to damage of the particles and formation of reaction products at the interface. This would prevent full realization of the strengthening potential of the composites. To avoid this, these composites are being made using solid state diffusion bonding technique (Singh *et al* 1993, 1994). Preliminary results indicate significant improvement in strength and modulus of the alloy with marginal drop in ductility.

Also, work is in progress to develop magnesium–lithium alloy with density of less than 1 g/cc. An alloy containing 50 wt.% lithium and 5 wt.% aluminium has

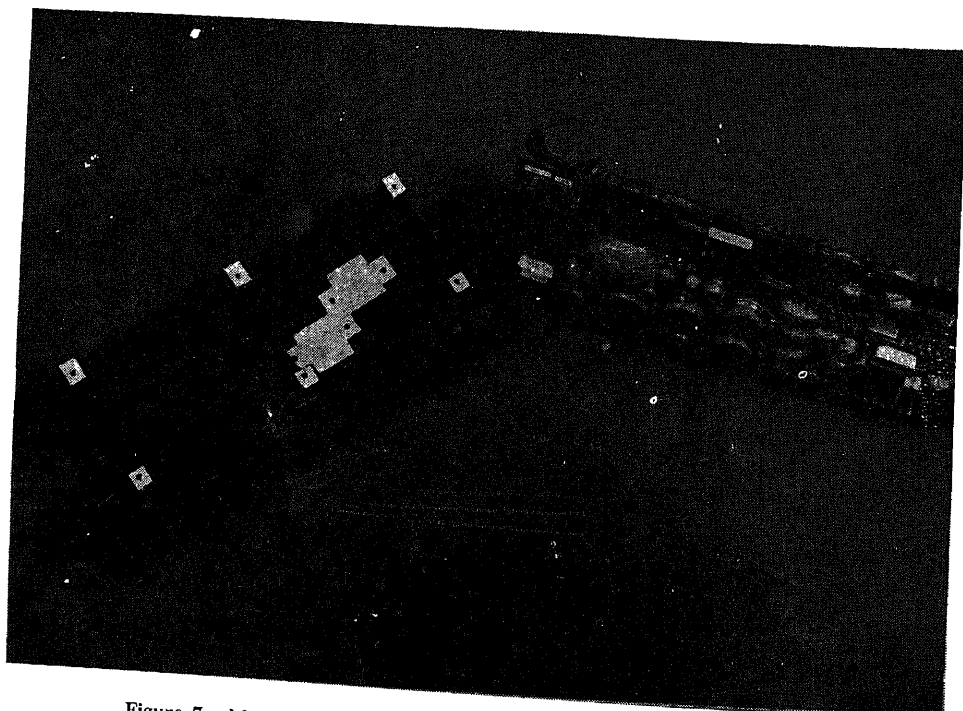


Figure 7. Magnesium-lithium alloy package box for INSAT-2.

been cast and processed to 2 mm thick sheets. At present, characterization of this alloy is being persuaded.

5. Summary

Sound cast ingots of magnesium-lithium alloys have been produced by optimizing melting and casting parameters of these alloys. Wrought products of varying thickness (0.5–60 mm) have been made and supplied to ISAC, Bangalore. Close association of Indian Satellite Application Centre, Bangalore during the development phase has helped in development of products with requisite properties sought and have found extensive application in INSAT-2 series. Figure 7 shows a typical component fabricated from magnesium-lithium alloy for INSAT-2.

Major limitations of the alloy i.e. instability of mechanical properties at room temperature and poor creep resistance have been overcome to a large extent by minor additions of zirconium. Magnesium-lithium composites having improved strength and modulus are being developed. The new improved alloy/composite shows potential for large scale exploitation as structural material in aerospace and allied industries. Interest shown by M/s Lockheed Company, USA for obtaining magnesium-lithium alloy sheets from DMRL also shows the export potential for this material.

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The hardness-flow stress correlation in metallic materials

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Abstract. Hardness is a measure of the resistance of a material to indentation and a wide variety of indentation tests have been devised to measure the hardness of materials. In the case of hardness tests which utilize spherical balls as the indenter, it is also possible to derive flow stress-strain relationships from hardness tests carried out either over a range of loads (static test) or over a range of impact velocities (dynamic test). This paper first describes the experimental procedure for obtaining stress-strain curves from hardness tests. In addition, the paper also analyzes in detail, the indentation test conditions under which the conversion of the hardness-average strain data to flow stress-strain data is simple and straightforward in the sense that the constraint factor which is the correlating parameter for the above conversion is not only independent of strain but also easily computable on the basis of known mechanical property data of the test material.

Keywords. Hardness-flow stress; static hardness; dynamic hardness; impact velocity; constraint factor Meyer hardness.

1. Introduction

Indentation tests carried out to measure the hardness of materials are usually referred to as hardness tests. Such tests usually involve the indentation of the test material with an indenter at a constant load (P) and the subsequent measurement of the dimensions of the indent that is formed on the test material. The hardness (H) is then obtained as,

$$H = P/A, \quad (1)$$

where A is the area of the indent formed on the test material. It is more appropriate and scientific to define A as the projected area of the indent rather than surface area, even though some of the well-known hardness tests usually define hardness in terms of the surface area of the indent. The hardness values obtained using projected area are usually distinguished from those obtained using surface area of the indent, by specifying the former as the projected area hardness (PAH).

The hardness tests can be classified either on the basis of the indentation test conditions (temperature and strain rate) or on the basis of the depth of indentation, as illustrated in figure 1. The well known conventional hardness tests, called static hardness in figure 1a, are carried out at around room temperature and the strain rate at which the plastic deformation of the test material occurs during indentation, lies in the range 10^{-3} to 10^{-1} s^{-1} . In contrast, dynamic hardness, involves strain rates in the range 10^3 to 10^5 s^{-1} . The hot hardness involves testing the material at temperatures in the range 0.4 to $0.8 T_m$ (T_m is the melting point of the test material) and at static strain rates (10^{-3} to 10^{-1} s^{-1}). The creep hardness (or impression creep)

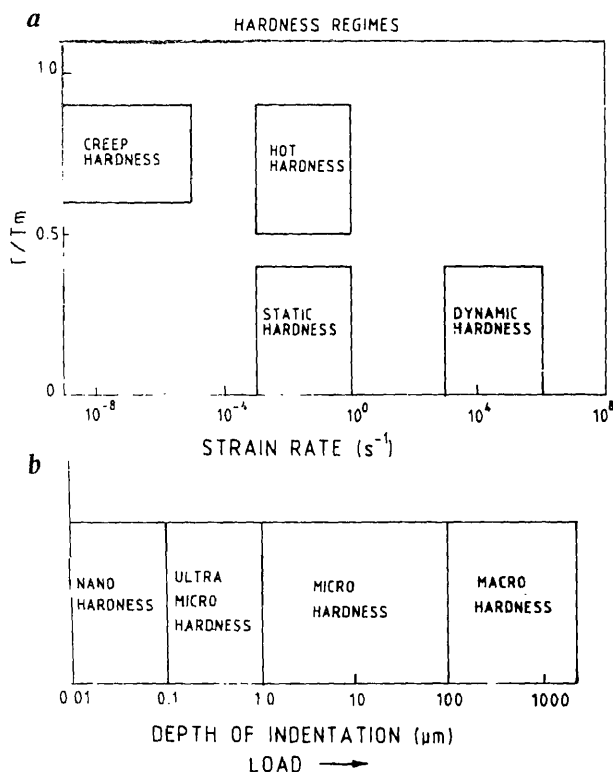


Figure 1. The classification of hardness tests on the basis of indentation test conditions (a) and depth of indentation (b).

is time dependent and is usually carried out for long times at temperatures above $0.4 T_m$ and at strain rates below $10^5 s^{-1}$ or so. All the hardness tests described above generally use indentation loads well in excess of 100 g and are classified as macrohardness tests. In such tests, the depth of indentation lies in the range 100 to a few thousand micrometers, as indicated in figure 1b. The microhardness tests wherein the indentation load lies in the range 1 to 100 g, are characterized by depth of indentation in the range 1 to 100 μm s. The nanohardness tests, wherein the test material is indented only up to a depth of 100 nm or less (figure 1b), represents the extreme case. Finally, the ultra microhardness tests, span the range in between that of nano and microhardness tests.

Apart from determining the hardness, the hardness tests can actually be used to obtain the plastic flow stress (σ)–plastic strain (ϵ) behaviour of materials (Tabor 1951; O'Neill 1967; Sundararajan and Shewmon 1983). The conditions under which the determination of the σ – ϵ curve using a hardness test becomes attractive, are listed below.

(i) The hardness test is a simple test and further requires samples having simple shapes. Thus, either when the sample size is limited because of the process technology involved or when the number of materials to be tested is large, the use of hardness test to obtain the σ – ϵ curve proves very effective.

variety of materials in order to improve their durability in service. The hardness test provides the only means to estimate the σ - ϵ behaviour of the coatings since by adjusting the indentation load, it can be ensured that only the coating is sampled during the hardness test. In this respect, the nano and ultra microhardness tests have proved extremely useful.

(iii) In the case of very brittle materials like ceramics, hardness test can be utilized to generate σ - ϵ curves since the presence of a substantial hydrostatic compressive stress during indentation postpones fracture to larger strains.

The conversion of hardness to flow stress, at a given constant strain, requires prior knowledge about the constraint factor (C). C is defined as,

$$C = H(\epsilon)/\sigma(\epsilon), \quad (2)$$

where H and σ are the hardness and flow stress at the same strain. A primary requirement for C is that it should be independent of strain. The present paper is concerned with providing a brief overview of the test and validation procedures involved in the determination of hardness-strain curves of metallic materials and their subsequent transformation to flow stress-strain curves. In particular, the test conditions under which the hardness test data can be effectively utilized for estimating the flow stress, is also highlighted.

2. Hardness-strain relationship

2.1 Introduction

During the indentation test, a plastic zone is formed underneath the indenter as illustrated in figure 2a. Within the plastic zone, there exists a plastic strain gradient (see figure 2b). The plastic strain which is maximum at the indenter-sample interface decreases continuously with increasing depth from the sample-indenter interface and ultimately reaches zero at the elastic-plastic boundary (figure 2b). Thus, an average or representative strain (ϵ_{av}) can be assigned to the plastic zone. In the case of spherical indentors, the magnitude of ϵ_{av} is determined by the dimensions of the indent formed while for conical and pyramidal indentors, the included angle of the indenter determines ϵ_{av} (Johnson 1985). Therefore, it follows that while the Vickers indenter induces a constant average strain of 8% ($\epsilon_{av} \approx 8\%$) irrespective of the load applied, in the case of spherical indenter the magnitude of ϵ_{av} depends on indent dimensions and hence on the applied load.

2.2 Test procedure

From the above discussion it is clear that a hardness (H)- ϵ_{av} relationship can be obtained only if spherical indentors are used. Therefore, a conventional Brinell hardness machine is usually utilized to obtain the H - ϵ_{av} relationship. Tungsten carbide (WC) balls of diameter 5 and 10 mm and test loads in the range 250 to 3000 kg are usually utilized for conducting the test. Flat specimens, 25 mm wide, 75 mm long and 15 mm thick and polished with emery paper to 600 grit size are used as the test samples for indentation.

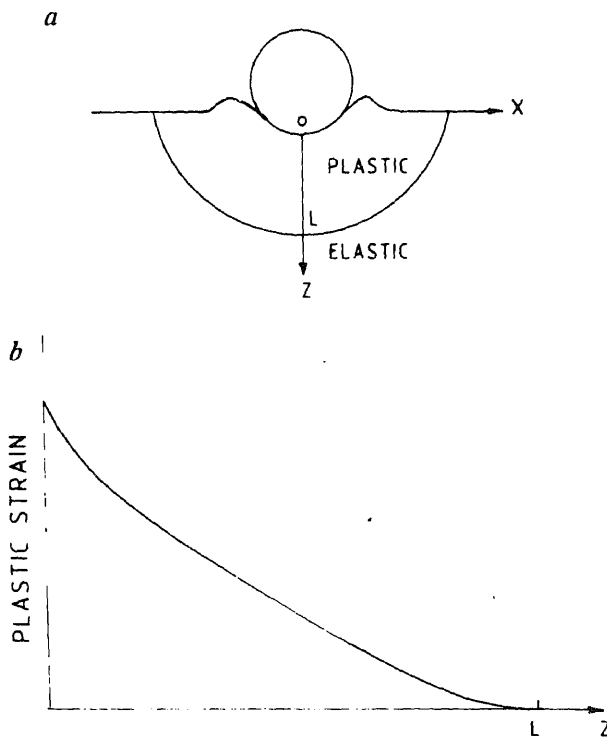


Figure 2. A schematic diagram illustrating the plastic zone formed beneath the indentation (a) and the plastic strain gradient within the plastic zone (b).

The indentation tests are carried out over a range of loads (L) and the diameter of the indent (W) so formed is measured using either an optical microscope or using a surface profile measuring equipment. The hardness (H_s) is then obtained as,

$$H_s = 4L/\pi W^2. \quad (3)$$

The most well-known expression for the average strain in the plastic zone (ϵ_{av}), due to Tabor (1951), is given as,

$$\epsilon_{av} = 0.2 (W/D). \quad (4)$$

In (4), D represents the ball diameter.

From (3) and (4) it is obvious that if the indentation tests are carried out over a range of loads, the hardness value can be obtained over a range of average strains. Thus, the H_s - ϵ_{av} relationship can be obtained.

The same concepts described above can be readily extended to the case wherein a WC ball impacts the test sample at considerable velocities (10 to 200 m/s) to obtain the dynamic hardness (H_d)- ϵ_{av} relationship. In the case of dynamic hardness experiments, indents of increasing dimensions (and hence increasing ϵ_{av}) are easily

obtained by impacting the sample with WC balls over a range of impact velocities. The value of H_d is obtained as (Tirupataiah and Sundararajan 1991a),

$$H_d = 0.5 mv^2 (1-e^2)/V_c, \quad (5)$$

$$V_c = \pi d^2 r (1 - (d/3r)), \quad (6)$$

$$d = r [1 - (1 - (W^2/4r^2))^{1/2}]. \quad (7)$$

In (5) to (7), m is the mass of ball, v the impact velocity, e the coefficient of restitution (see Tirupataiah *et al* (1990) for more details), V_c the indent volume, r the ball radius, W the indent diameter and d the maximum indent depth during impact. The average strain (ϵ_{av}) is determined by (4) given earlier, even under dynamic impact conditions. Thus, using (4) to (7), H_d - ϵ_{av} relationship can be obtained for a given test material.

The major difference between the dynamic and static hardness tests (i.e. H_d and H_s) lies in the fact that the strain rate at which the plastic deformation occurs in the plastic zone (in the sample) during the two tests are vastly different. While the strain rates are around 10^{-3} to 10^{-2} s^{-1} in the static tests, the corresponding strain rates in the dynamic tests lie in the range 10^3 to 10^4 s^{-1} (Tirupataiah *et al* 1991a). The strain rates are thus 6 orders of magnitude higher during dynamic indentation as compared to static indentation.

2.3 Results

The variation of dynamic and static hardness with average strain, as obtained using the techniques described in § 2.2, are illustrated for Cu and Cu alloys, iron and steel and Ni and Ni base alloys in figures 3, 4 and 5 respectively. In all these figures, the filled circles represent the dynamic data while the unfilled circles correspond to the static data. For all the materials illustrated in figures 3-5 (i.e. Cu, Cu-Zn, Cu-Al, Fe, Hv 260 steel, Ni, Ni-20 Cr and MA 754 alloy) the dynamic hardness- ϵ_{av} curve clearly lies above the static hardness- ϵ_{av} curve pointing to the fact that the hardness of all these materials exhibit a positive strain rate sensitivity with regard to strength.

The ratio of dynamic to static hardness (i.e. H_d/H_s) at a constant strain of 7% is presented in figure 6a for a number of metallic materials. In the case of pure metals like Al and Fe, H_d is more than twice H_s pointing to extreme strain rate sensitivity. In the case of the other materials, as can be noted from figure 6a, H_d is about 20 to 40% higher than H_s .

The dynamic and static hardness- ϵ_{av} curves are usually fitted to equations of the following form

$$H_s = H_{os} \cdot \epsilon_{av}^{n_s}, \quad (8)$$

$$H_d = H_{od} \cdot \epsilon_{av}^{n_d}. \quad (9)$$

In (8) and (9), H_{os} and H_{od} represent the static and dynamic hardness coefficients and n_d and n_s correspond to the dynamic and static strain hardening exponents respectively. The ratio H_{od}/H_{os} , for a number of metallic materials, is presented

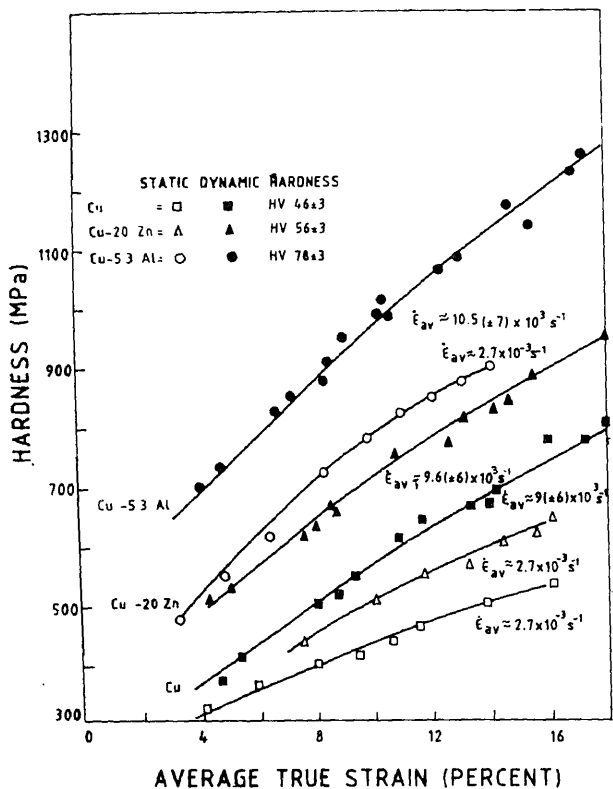


Figure 3. Variation of static and dynamic hardness as a function of average true strain for Cu, Cu-20% Zn and Cu-5.3% Al alloys.

in figure 6b. The trend of the data is broadly similar to that of the ratio H_d/H_s (figure 6a). The only significant difference is that in the case of precipitation and dispersion hardened alloys like Al 7039 and MA 754, the ratio $H_{od}/H_{os} < 1$. Since, H_{od} and H_{os} are characteristic of material strength at large strains, the implication is that the positive strain rate sensitivity with respect to hardness disappears or even becomes negative at large strains.

In figure 7, the n_d and n_M values (defined by (8) and (9)) are compared for a variety of metallic materials. In the case of pure fcc metals like Ni and Cu, $n_d > n_M$ and thus these materials exhibit increased strain hardening capability at dynamic strain rates. Solid solutions of fcc metals (Cu-Zn, Cu-Al, Ni-Cr and Al 7039 alloy) are characterized by nearly the same n_M and n_d values. In contrast, bcc metals (Fe) and dispersion strengthened alloys (MA 754) exhibit a lower strain hardening capability at dynamic strain rates, i.e. $n_d < n_M$. Pure Al, though a fcc metal, also behaves like a bcc metal most probably due to its high stacking fault energy (unlike Cu or Ni).

2.4 Assumptions and their validity

2.4a Tabor relation for average strain: In the case of both the static and dynamic

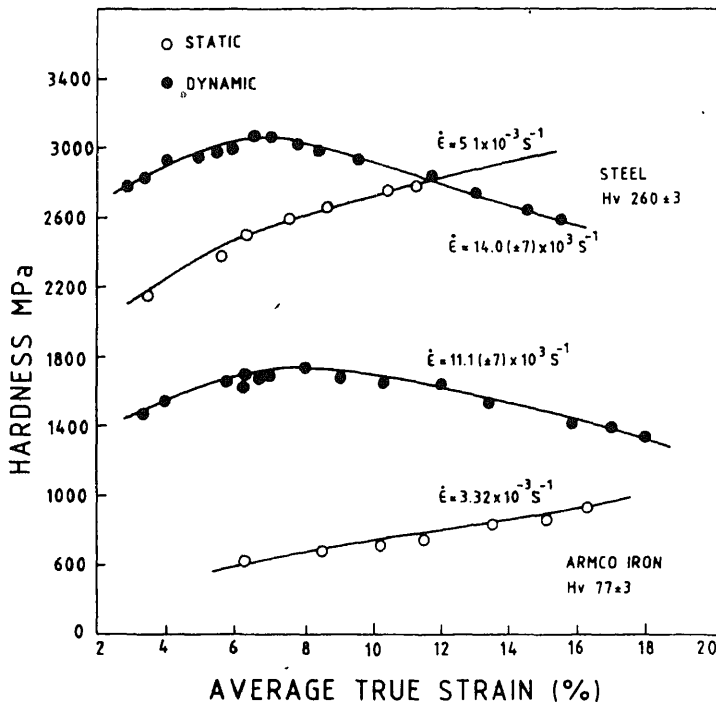


Figure 4. Variation of static and dynamic hardness as a function of average true strain for iron and steel B1 (Hv 260).

hardness tests, a key assumption is that the Tabor relation (4) can be utilized for estimating the average strain (ϵ_{av}) in the plastic zone formed underneath the indenter. The above assumption is shown to be valid, in this section on the basis of a simple energy-based analysis.

Assume the shape and size of the plastic zone formed beneath the indent, in the test material, as illustrated in figure 8. The plastic zone can be modelled with adequate accuracy as a hemisphere of radius $\beta (W/2)$ (W , indent diameter). If we further assume the following constitutive equation for plastic flow,

$$\sigma = K \epsilon_{av}^n, \quad (10)$$

where σ is the flow stress, ϵ_{av} the plastic strain, K the strength coefficient and n the strain hardening exponent, then the energy dissipated in the plastic zone (E_{pl}) through plastic flow is obtained as (Tirupataiah and Sundararajan 1991b),

$$E_{pl} = (\pi/12) \beta^3 W^3 K \epsilon_{av}^n / n + 1. \quad (11)$$

The energy expended by the indenter as it forms the indent (E_{ind}) is given as (Tirupataiah and Sundararajan 1991b),

$$E_{ind} = C \cdot K \epsilon_{av}^n (\pi W^4 / 32D), \quad (12)$$

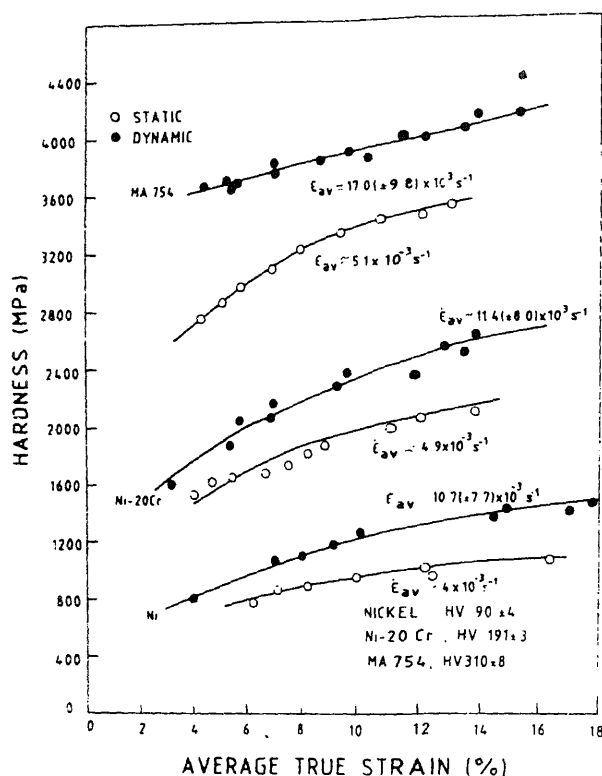


Figure 5. Variation of static and dynamic hardness as a function of average true strain for Ni, Ni-20% Cr and MA 754 alloy.

where C is the constraint factor defined earlier (2), D the ball diameter and the term within the brackets represents the indent volume. Since (11) and (12) should be equal to each other, ϵ_{av} can be obtained as,

$$\epsilon_{av} = (3/8) [C(n+1)/\beta^3] (W/D). \quad (13)$$

It can be seen that (13) is identical to the Tabor relation (4) and in fact gives additional information on the parameters which have bearing on the numerical constant of 0.2 in (4). The main conclusion from the above analysis is that as long as the plastic zone scales as the indent diameter, the Tabor relation for ϵ_{av} should be valid.

In figure 9, the variation of the parameter β ($= (L_1 + 0.5 W)/0.5 W = (L_2 + d)/0.5 W$, see figure 8) with ϵ_{av} is plotted for a large number of materials. The values of L_1 and/or L_2 were measured for each indent either through lip height measurements using surface profilometer or through microhardness-depth profiles carried out on surfaces sectioned perpendicular to and along the diameter of the indent (Tirupataiah and Sundararajan 1987). The filled and unfilled symbols represent the β values measured on dynamically and statically formed indents respectively. It is clear from figure 9 that β is, to a very good approximation, independent of both ϵ_{av} and the

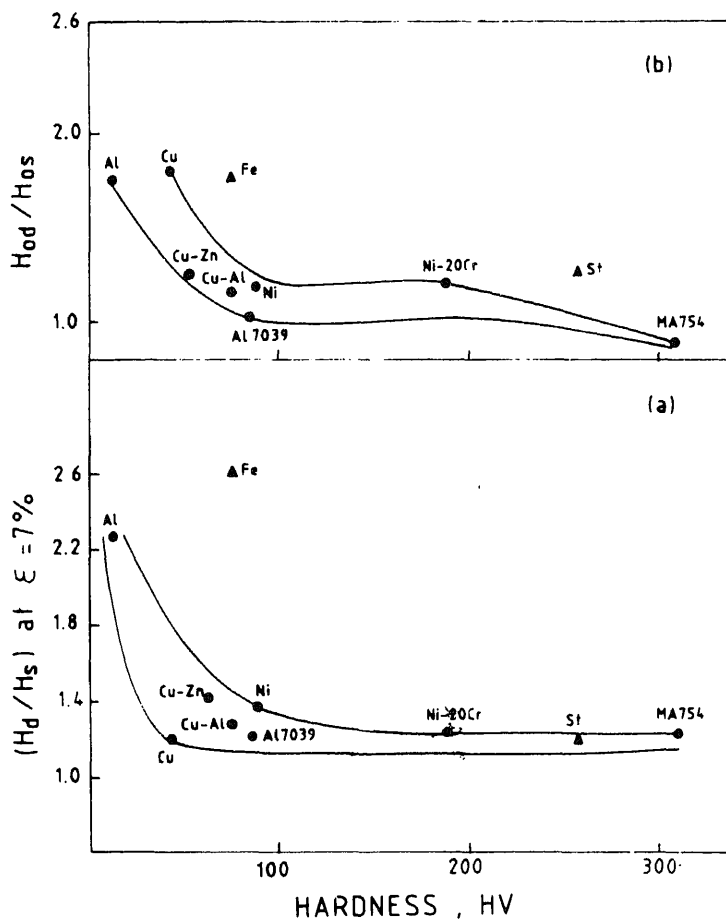


Figure 6. (a) The ratio of dynamic to static hardness (H_d/H_s) at a constant strain of 7% for a number of metallic materials and (b) the ratio H_{0d}/H_{0s} (defined by (8) and (9) in the text) for a number of metallic materials.

test material. Figure 9 thus demonstrates the validity of the Tabor relation for ϵ_{av} (4) under both static and dynamic indentation conditions.

2.4b Negligible deformation of the ball: Under static indentation conditions, it is well known that the ball hardness should be atleast twice the hardness of the test material, for a valid hardness test. In contrast, under dynamic indentation conditions, it is not clear as to how much harder the impacting ball should be in comparison to the hardness of the test material. To answer the question, a series of dynamic indentation tests were carried out with a variety of balls (WC, steel, ceramic and nylon) having a wide range of hardness (Hv 9 to Hv 1018) (Tirupataiah and Sundararajan 1990). A steel of hardness Hv 551 was used as the test material and indentations were carried out over a range of impact velocities. For each of the indentation tests carried out, the crater volume (V_c), dynamic hardness (H_d) and average strain (ϵ_{av}) were determined using (5), (6) and (4) respectively. The results

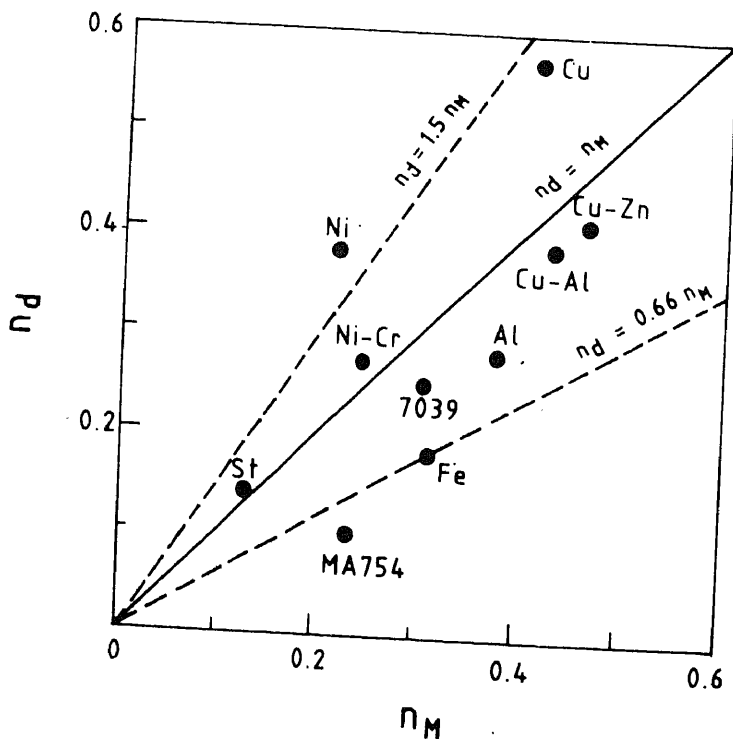


Figure 7. A comparison of static and dynamic strain hardening exponents (n_M and n_d respectively) for a number of metals and alloys.

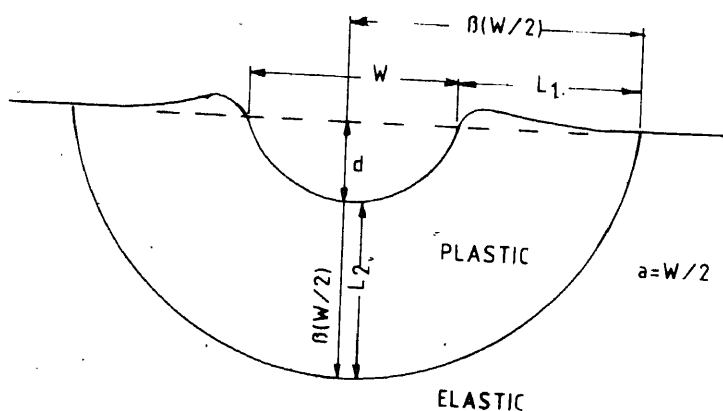


Figure 8. A schematic diagram of the plastic zone with the various parameters defined.

are presented in figure 10. The variation of the normalized crater volume with the ratio of the hardness of the ball to that of the test material is illustrated in figure 10a for various constant values of kinetic energy of the impacting ball. Similarly, the ratio H_d (different ball) / H_d (WC ball) is plotted against H_v (ball) / H_v (test

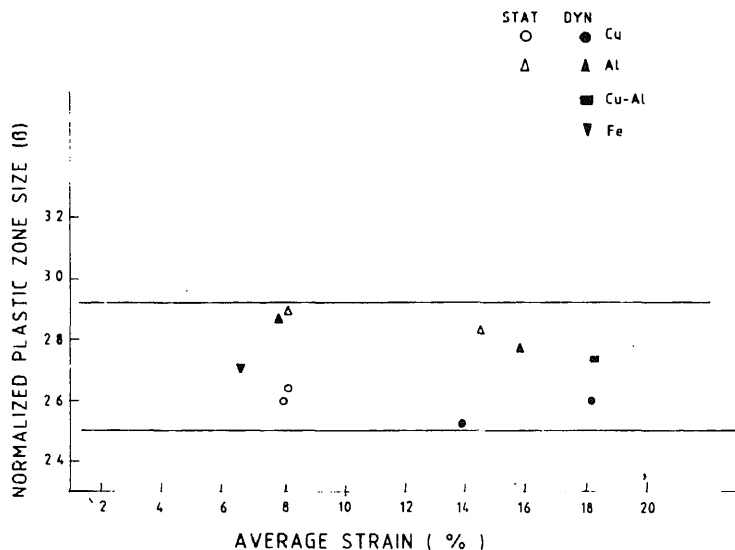


Figure 9. The variation of the normalized plastic zone size (β) with average strain (ϵ_{av}) for a number of materials. The filled and unfilled symbols represent dynamic and static indentation data respectively.

material) in figure 10b at various constant levels of ϵ_{av} . It is clear from both the figures 10a and b that if the hardness of the ball is less than about 1.5 times the hardness of the test material, the crater volume shows a decrease and correspondingly H_d shows a dramatic increase with decreasing hardness ratio. Such a trend in data is consistent with the ball undergoing plastic deformation during indentation. Thus, it can be concluded that the rule of thumb valid for static hardness tests, viz. that the hardness of the ball should be atleast twice the hardness of the test material, is equally valid for dynamic hardness tests.

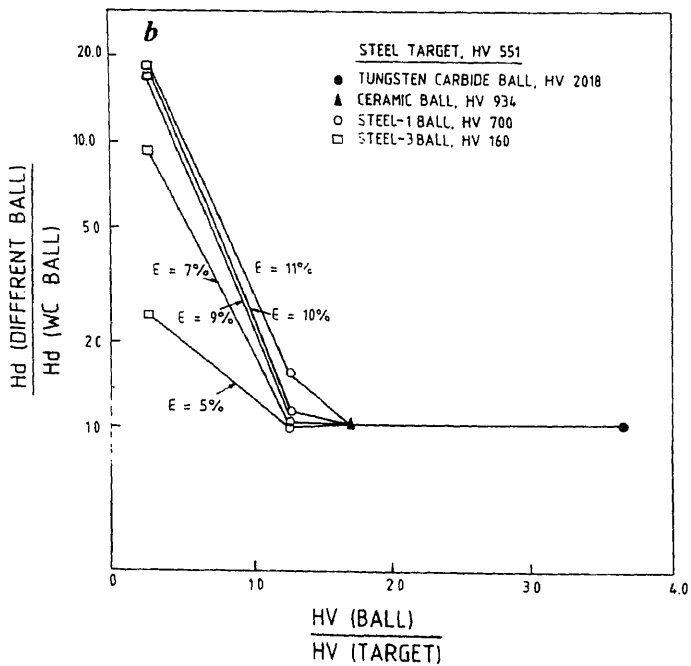
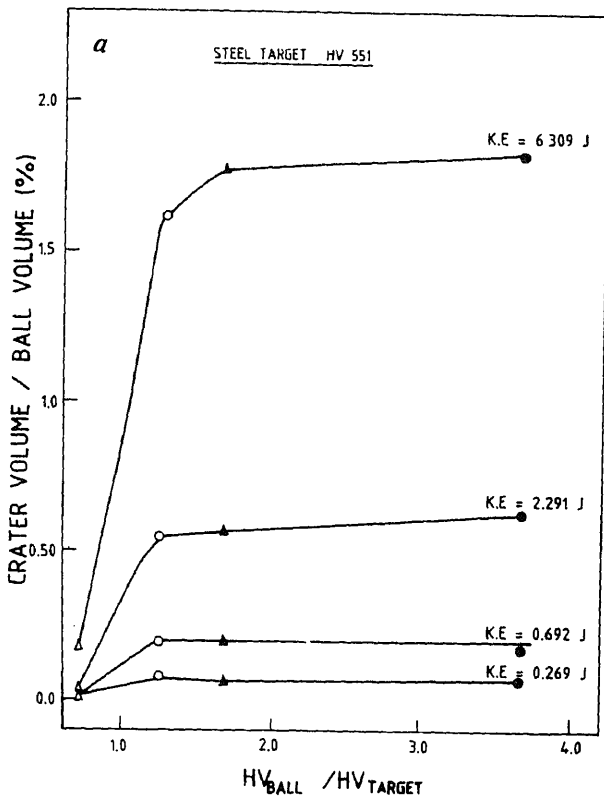
3. Flow stress-strain relationship

3.1 Introduction

In the last section, the procedure for obtaining the hardness-strain relationship in the case of metallic materials was described. The transformation of H - ϵ_{av} curves to flow stress (σ)-strain (ϵ) curves requires information on the constraint factor (C) described earlier (2). The relationship between the H - ϵ_{av} and σ - ϵ curves is schematically illustrated in figure 11. Thus, H and σ are related to each other, at a given strain (ϵ) given below

$$H(\epsilon) = C \sigma(\epsilon). \quad (14)$$

Ideally, C should be independent of strain for a given material as shown in figure 11. Further, if C is also reasonably independent of the test material properties, then a constant value for C can be used to convert the H - ϵ curve of any material



to the corresponding flow stress-strain curve. In fact, many of the investigators have made such an assumption and have utilized a value in the range 2.8 to 3 for C (Francis 1976). But as will be shown subsequently, C is not really independent of the test material properties and further under certain indentation conditions, C is also a function of strain. Therefore, it is important that the indentation test conditions under which the concept of the constraint factor can be effectively utilized to obtain σ - ϵ curves, be clearly defined and demarcated.

3.2 Experimental determination of C

To investigate the dependence of the constraint factor (C) on strain and test material properties, C has to be experimentally determined through independent hardness and tensile/compression tests on the same material. As illustrated in figure 11, if H_s - ϵ_{av} curve is determined using hardness test and the σ - ϵ relation through tensile or compression tests, C can be determined at different constant levels of strain.

Figures 12 and 13 illustrate the experimental H_s - ϵ_{av} and σ - ϵ curves in the case of copper and iron respectively. In these figures, the full line joining the unfilled circles represent the H_s - ϵ_{av} curve while the full line and the dashed line represent the compressive and tensile σ - ϵ curves respectively. As to be expected, the tensile and compressive σ - ϵ curves lie very close to each other. In the same figures 12 and 13, the filled circles represent the σ points obtained by dividing H_s by C where C equals 2.42 for Cu and 2.61 for iron. It is clear that the σ values obtained by assuming a constant value for C , independent of strain, correspond very well with the σ - ϵ curves obtained from tensile and compression tests.

3.3 Constraint factor and strain

In the case of copper and iron, the constraint factor (C) appears to be independent of strain as can be noted from figures 12 and 13. However, the above assumption does not hold for a number of test materials as can be observed from figures 14, 15 and 16. In each of these figures, C is plotted as a function of ϵ_{av} . In the case of Cu, Cu-Zn and Cu-Al alloys, C is independent of strain (figure 14). In contrast, in the case of steels (figure 15), C increases with increasing strain at low strains but becomes independent of strain at large strains. In the case of an Al 7039 alloy, C is independent of strain when the alloy is tested in the solution treated condition (figure 16c). However, in the aged and overaged conditions, C increases with strain at low strains and then becomes a constant (figures 16a and b).

On the basis of the C - ϵ behaviour illustrated in figures 14 to 16, a transition strain (ϵ_{tr}) can be defined. For $\epsilon < \epsilon_{tr}$, C increases with increasing strain while for $\epsilon \geq \epsilon_{tr}$, C is independent of strain. The above transition behaviour is related to the

Figure 10. (a) The variation of crater volume normalized by the ball volume as a function of the ratio ball hardness to target hardness for a steel target at four different constant kinetic energy values and (b) the variation of dynamic hardness of steel target obtained using different balls normalized by the dynamic hardness obtained using WC ball, as a function of the ratio of the ball hardness to target hardness, for WC, ceramic, steel 1 (Hv 700) and steel 3 (Hv 160) balls.

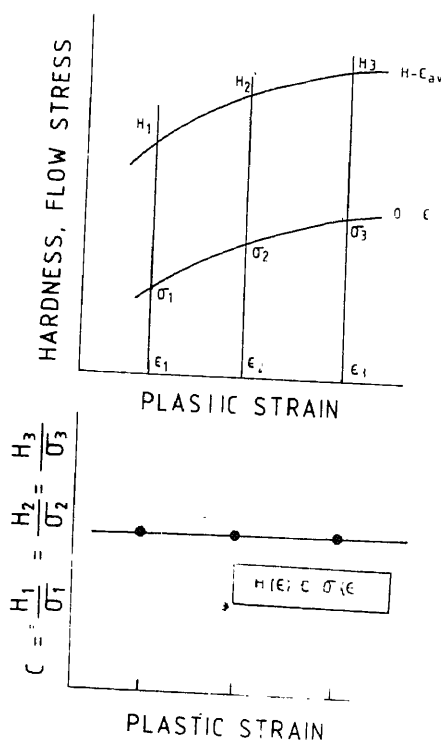


Figure 11. A schematic diagram illustrating the relationship between the H - ϵ_{av} and the σ - ϵ curves through the constraint factor (C).

transition of the valid indentation model from the elastic-plastic model at low strains ($\epsilon < \epsilon_{tr}$) to the fully plastic model at large strains ($\geq \epsilon_{tr}$). An expression for the above transition strain (ϵ_{tr}) can be obtained as (Tirupataiah and Sundararajan 1991b),

$$\epsilon_{tr} = (9K/E_e)^{1/(1-n)} \quad (15)$$

In (15), K and n are defined by (10) and E_e is the effective modulus of the indenter-test material system and is given as,

$$E_e = EE_b/[E(1-\nu_b) + E_b(1-\nu^2)] \quad (16)$$

In (16), E and ν are the elastic modulus and Poissons ratio respectively of the test material while E_b and ν_b are the corresponding values for the ball material. To conclude, as long as the average strain introduced in the plastic zone exceeds ϵ_{tr} , it is reasonable to assume a strain independent value for C .

3.4 Constraint factor and material properties

In the last section it has been shown that for any test material, an appropriate

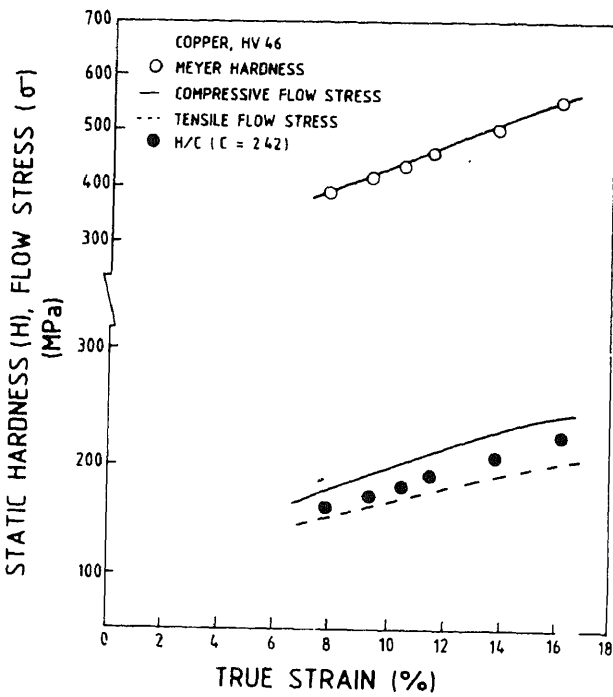


Figure 12. The experimental H_s - ϵ_{av} and σ - ϵ curves for copper. The filled circles represent the σ - ϵ data derived from H_s - ϵ_{av} curve.

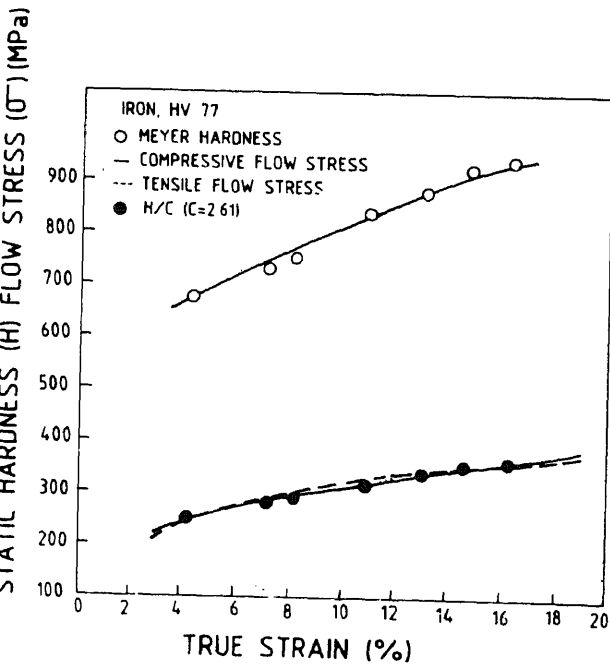


Figure 13. The experimental H_s - ϵ_{av} and σ - ϵ curves for iron. The filled circles represent the σ - ϵ data derived from H_s - ϵ_{av} curve.

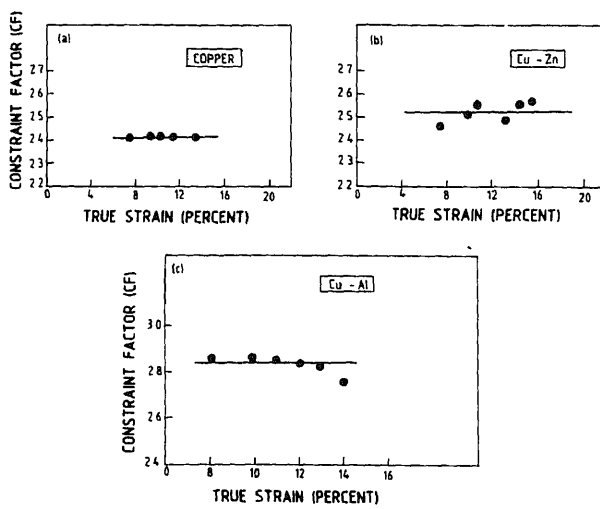


Figure 14. The variation of constraint factor with average true strain: (a) copper, (b) Cu-Zn alloy and (c) Cu- Al alloy.

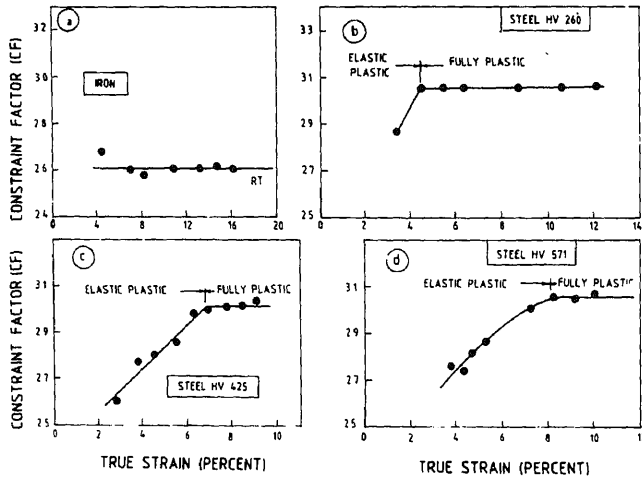


Figure 15. The variation of constraint factor with true strain: (a) iron, (b) steel, Hv 260; (c) steel, Hv 425; and (d) steel, Hv 571.

strain regime ($> \epsilon_{ir}$) can be defined wherein C is independent of strain. The next question is related to the magnitude of C (for $\epsilon \geq \epsilon_{ir}$) and the manner in which the test material properties (like K and n) influence C .

In table 1, the value of C (for $\epsilon \geq \epsilon_{ir}$) is listed for 16 test materials along with their mechanical property values. The first point to be noted from table 1 is that the value of C varies from 2.25 for Al to 3.06 for steel of hardness Hv 571. Thus, C is certainly a material dependent parameter.

To elucidate more clearly the influence of material parameters on C , the variation of C with the strain hardening exponent (n) is presented in figure 17. The

experimental values of C (from table 1) are indicated as filled circles while the value of C predicted by the equation due to Mathews (1980), given below is represented by the full line

$$C = (3/1 + 0.5n) (1.415)^n. \quad (17)$$

It is clear from figure 17 that majority of the data points fit (17). However, there

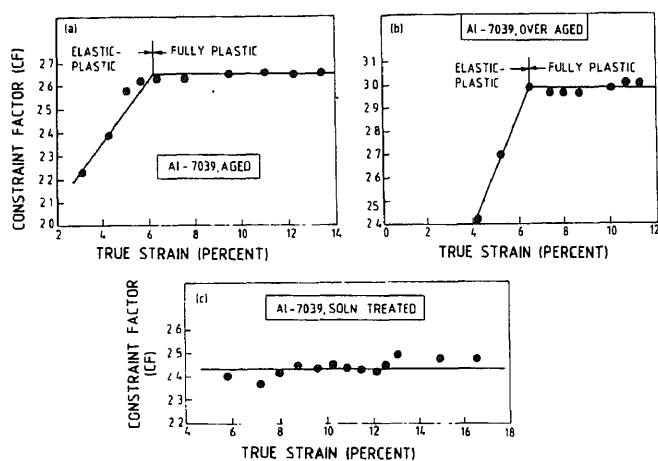


Figure 16. The variation of constraint factor of an Al 7039 alloy with true strain: (a) aged, (b) overaged and (c) solution treated.

Table 1. The experimentally obtained constraint factors and mechanical properties.

Material	Hardness (Hv; kg/mm ²)	Constraint factor (C)	K (MPa)	n
Copper (Cu)	46 ± 3	2.41	512	0.45
Cu-20 Zn	56 ± 2	2.52	595	0.485
Cu-5.3 Al	78 ± 3	2.84	915	0.52
Nickel (Ni)	90 ± 4	2.87	490	0.20
Iron	77 ± 3	2.61	568	0.26
Steel A 1	314 ± 3	2.93	1300	0.096
Steel A 2	356 ± 6	2.92	1375	0.07
Steel A 3	487 ± 6	2.90	1860	0.049
Steel A 4	569 ± 8	3.01	2213	0.056
Steel B 1	260 ± 3	3.06	1137	0.12
Steel B 2	425 ± 5	3.00	1534	0.061
Steel B 3	571 ± 6	3.06	2163	0.05
Al	14 ± 1	2.25	135	0.28
Al 7039 (ST)	86 ± 2	2.44	605	0.268
Al 7039 (PA)	169 ± 3	2.96	693	0.061
Al 7039 (OA)	112 ± 3	2.62	508	0.115

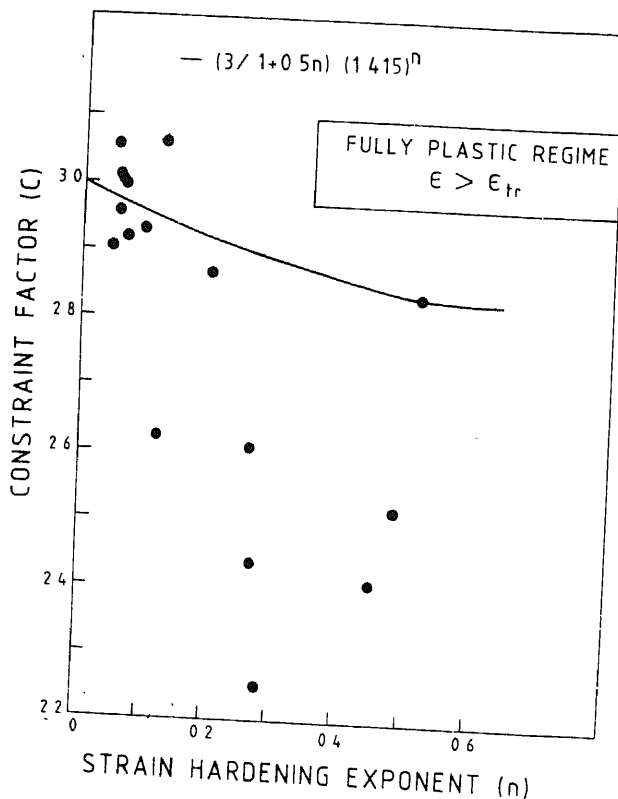


Figure 17. The variation of constraint factor (C) with strain hardening exponent (n). The value of C predicted by Mathews ((17) in the text) is represented by the full line.

are 6 data points which lie well below the theoretical line. A perusal of these data points indicate that they pertain to materials with low K values (see table 1) like Cu, Al, Fe, Cu-Zn, Al-7039 (ST) and Al-7039 (OA). To observe the effect of K per se on C more clearly, in figure 18, the ratio of experimental to predicted (17) value of C is plotted as a function of K . Figure 18 brings out the K effect very clearly and in fact suggests that K has an influence on C only when $K \leq 900$ MPa.

The influence of n and K , demonstrated by figures 17 and 18, can be combined to give the following empirical expressions for C .

$$C = (3/1 + 0.5n) (K \text{ (MPa)} / 900)^{n/2} (1.415)^n \text{ for } K < 900 \text{ MPa,} \quad (18)$$

$$C = (3/1 + 0.5n) (1.415)^n \text{ for } K \geq 900 \text{ MPa.} \quad (19)$$

The values of C predicted by (18) and (19), for all the test materials listed in table 1, is compared with the corresponding experimental values of C in figure 19. In this figure the diagonal line represents the perfect matching between the predicted and experimental values. It is obvious from figure 19 that (18) and (19) have the capability to predict C values for a wide range of materials within $\pm 10\%$.

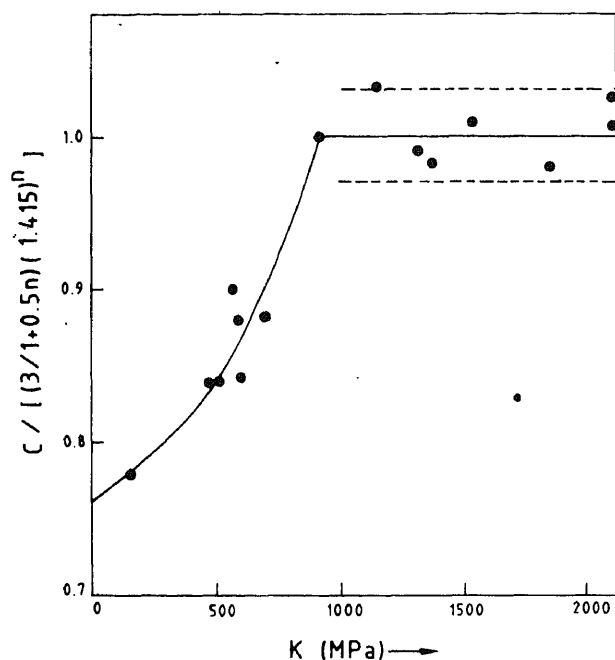


Figure 18. The variation of the ratio of experimental value of C (table 1) to the predicted value of C (17) with the strength coefficient (K).

3.5 Constraint factor at high strain rates

All the discussions pertaining to C has so far dealt with only static indentation tests. On the other hand, it is not clear as to whether the concepts related to C , developed in §§ 3.2 to 3.4, are equally valid under dynamic indentation conditions. It is demonstrated below, albeit in an indirect fashion, that the concepts related to C are indeed valid even under high strain rate deformation conditions characteristic of dynamic indentation.

In figure 20, the microhardness–depth profiles measured on surfaces, obtained by sectioning the indent formed on the test material along its diagonal, are presented for both static and dynamic indentations in the case of iron and copper. The main point to be noted in figure 20 is that the microhardness–depth profiles are nearly identical for both static and dynamic indents when the comparison is made at nearly the same average strain. Thus, it can be concluded that not only the size of the plastic zone (defined as L in figure 20) but also the strain distribution within the plastic zone are identical irrespective of whether the indentation occurs under static or dynamic conditions. Figure 9, wherein the size of the normalized plastic zone is indicated for both static and dynamic indentations, also provides additional proof for the statement that the plastic zone size does not depend on whether the indentation is done under static or dynamic conditions. Since the energy dissipated in the plastic zone during indentation is largely a function of the plastic zone size and the strain distribution within the plastic zone (for a given material), it follows that C should not be dependent on the indentation rate (i.e. static or dynamic).

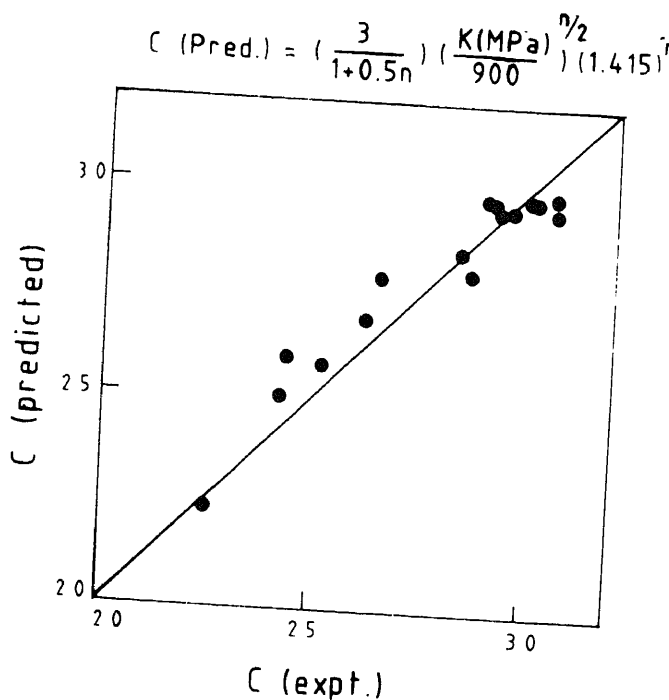


Figure 19. A comparison of the experimental value of C (table 1) with the value of C predicted by the empirical equations ((18) and (19) in the text) in the case of a number of metallic materials.

In figure 21, the variation of the flow stress (σ) of Cu with strain (ϵ) is presented. The solid lines represent the static and dynamic σ - ϵ curves of Cu derived from static and dynamic indentation tests respectively. The dashed line represents the static and dynamic σ - ϵ curves of Cu obtained by Follansbee and Kocks (1988) utilizing tensile test and split Hopkinson pressure bar test respectively. The figure shows that the σ - ϵ curves derived from indentation tests compare very well with the data of Follansbee and Kocks (1988). Since the same value of 2.41 was used for C while deriving both the dynamic and static σ - ϵ curves from the corresponding hardness-strain curves, the data presented in figure 21 provides additional proof for our assumption that C is not a function of indentation rate.

In the case of static indentations, C is independent of strain for $\epsilon > \epsilon_{tr}$ (15). A similar condition applies for dynamic indentations as well. However, an additional restriction manifests itself during dynamic indentation. As demonstrated elsewhere (Tirupataiah and Sundararajan 1991a), beyond a critical strain (ϵ_c), the plastic zone starts decreasing in size with increasing strain due to the onset of localization of plastic flow. Once the localization of plastic zone occurs, the H_d - ϵ curve which usually increases with increasing strain shows a downturn (see figure 5 for example) and the constraint factor also starts decreasing. Further, the Tabor relation for ϵ_{av} is no longer applicable under such conditions. As shown in an earlier publication (Tirupataiah and Sundararajan 1991a), the expression for ϵ_c is obtained as;

$$\epsilon_c = [nA/C]^{1/n+1}; A = p_t C_p T_m/K.$$

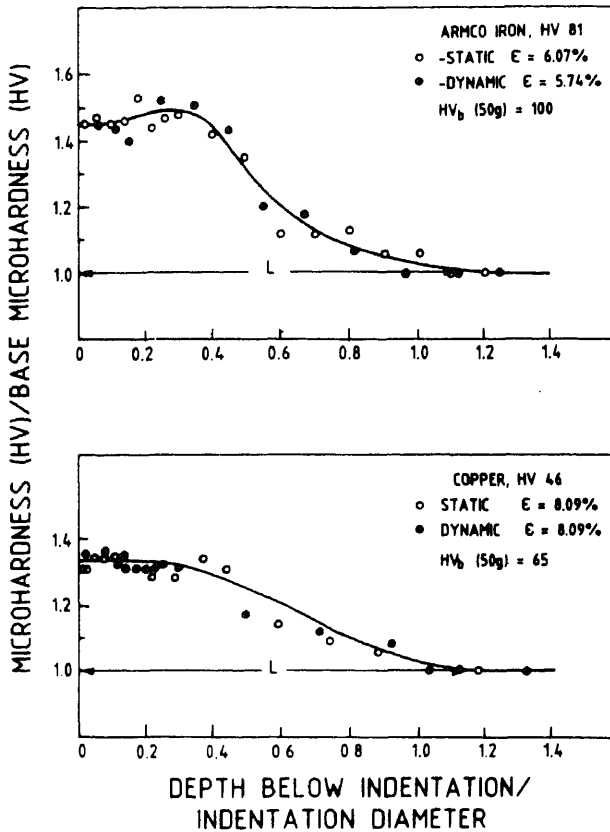


Figure 20. The microhardness–depth profiles obtained on statically and dynamically indented samples of iron and copper. In each of these profiles, the filled and unfilled symbols represent microhardness data obtained on dynamically and statically indented samples to nearly the same average strain.

In (20), C is the normalized temperature dependence of flow stress (~ 0.5 for many metals) and ρ_i , C_p and T_m represent the density, specific heat and melting point respectively of the test material. In figure 22, the values of ϵ_c predicted by (20) is presented for a number of metallic materials. In general, lower the K value and higher the n value, higher is the ϵ_c value.

3.6 Test conditions for strain independent C

In earlier sections, it has been shown that the average strain induced during indentation (static or dynamic) should exceed ϵ_{tr} (15) for C to be independent of strain. In the case of dynamic indentation, an additional constraint for $C \neq f(\epsilon_{av})$ is that ϵ_{av} should be less than ϵ_c for localization (20). In figure 23, the computed values of ϵ_{tr} (using (15)) and the experimental values of ϵ_c (from Tirupataiah and Sundararajan 1991a) are indicated in the form of bar graphs for a number of metallic materials.

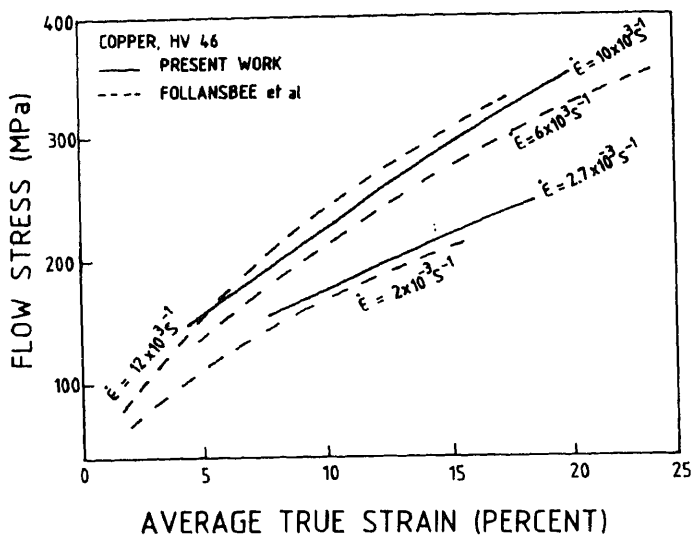


Figure 21. A comparison of the present dynamic and static data (full lines) for copper with that of Follansbee *et al* (dotted lines).

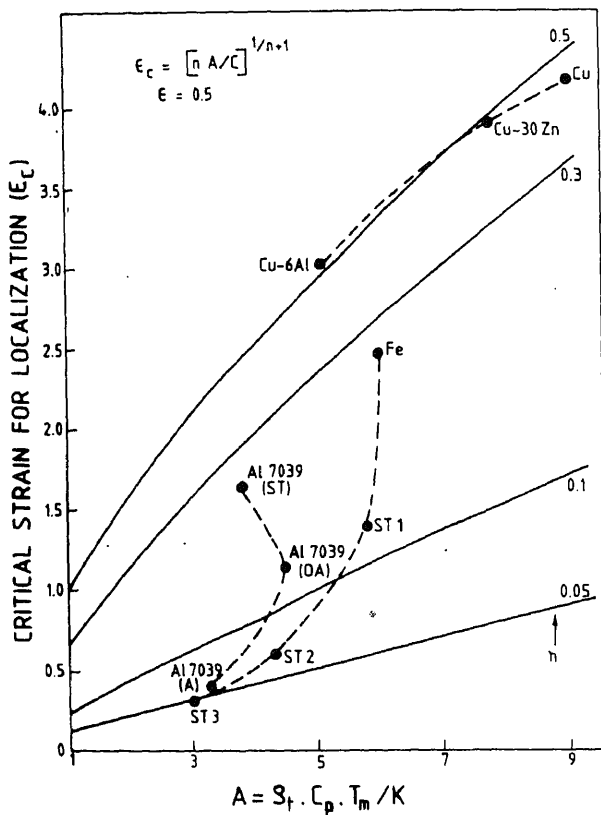


Figure 22. The variation of ϵ_c predicted by (20) as a function of parameter A for a number of test materials.

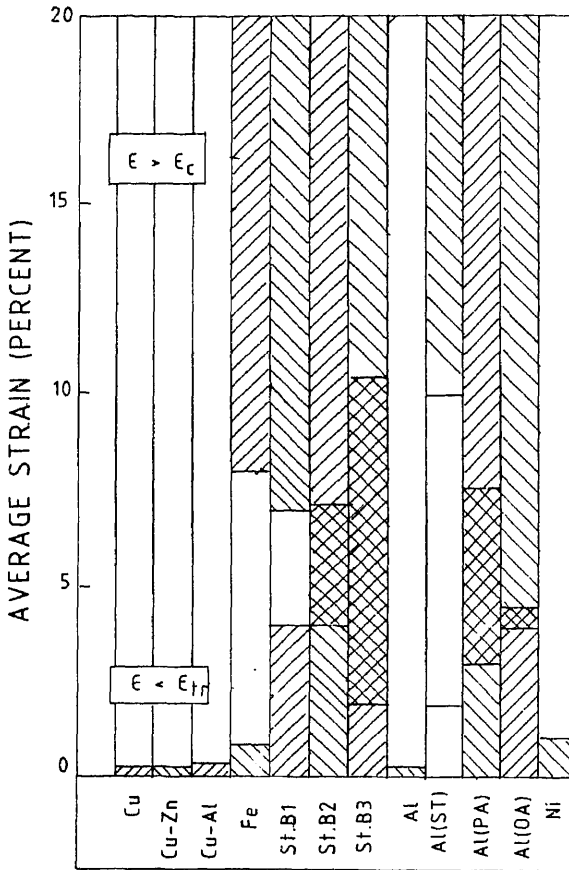


Figure 23. The computed values of ϵ_{tr} (9) and the experimental values for ϵ_c for a number of metals and alloys. Each bar in the figure represents one material.

If static indentation conditions are considered, ϵ_{av} should exceed ϵ_{tr} for obtaining strain independent C . From figure 23, it is clear that ϵ_{tr} varies quite widely depending on the test material properties. The value of ϵ_{tr} is lower than 1% in the case of metals and alloys like Cu, Cu-Zn, Cu-Al, Fe, Al and Ni. In contrast, in the case of steels and Al alloy in the peak and overaged conditions, ϵ_{tr} exceeds 1% and becomes as high as 10.6% in steel with a hardness of Hv 571.

A strain independent value for C is possible under dynamic conditions only if $\epsilon_{av} < \epsilon_c$ in addition to the other condition $\epsilon_{av} > \epsilon_{tr}$. In figure 23, the experimental values of ϵ_c are also indicated except for cases where ϵ_c exceeds 20%. Strains beyond 20% are not considered since the indentation technique is not capable of inducing average strains in excess of 20%. Thus, for each material represented as a bar in figure 23, the portion of the bar which remains unshaded represents the useful ϵ_{av} regime wherein a strain-independent C value can be obtained under dynamic indentation conditions. A perusal of figure 23, with the above definition in mind, indicates that the useful ϵ_{av} regime is large for materials like Cu, Cu-Zn, Cu-Al, Al and Ni. In the case of materials like Fe, steel B1 (Hv 260) and Al alloy (ST condition), the useful ϵ_{av} regime is quite restricted (e.g. between 1 and 8%

for iron and between 4 and 7% for steel B1). Finally, in the case of steels B2 (Hv 425) and B3 (Hv 571) and Al alloy in peak aged and overaged conditions, an useful ϵ_{av} regime does not exist under dynamic indentation conditions. Thus, for such alloys, the hardness test should not be utilized to derive the flow stress-strain relationship.

4. Conclusions

In this paper, the correlation that exists between hardness and flow stress in metallic materials, has been examined in detail. The experimental procedure for deriving flow stress-strain relationship from static or dynamic hardness tests using the constraint factor approach has been described. In particular, the indentation test conditions required for obtaining a strain independent constraint factor has been analyzed for both static and dynamic indentation conditions. In addition, it has been demonstrated that even under test conditions wherein C is independent of strain, the test material parameters (like K and n) does influence the magnitude of C . An empirical relation which accounts adequately for the influence of material properties on C , has been proposed.

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Formation and propagation of bands in jerky flow: coupled lattice map description*

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Abstract. There has been revival of interest in Jerky flow from the point of view of dynamical systems. The earliest attempt in this direction was from our group. One of the predictions of the theory is that Jerky flow could be chaotic. This has been recently verified by us. We have recently extended the earlier model to account for the spatial aspect as well. Both these models are in the form of coupled set of nonlinear differential equations and hence, they are complicated in their structure. For this reason we wish to devise a model based on the results of these two theories in the form of coupled lattice map for the description of the formation and propagation of dislocation bands. We report here one such model and its results.

Keywords. Jerky flow; Portevin-Le Chatelier effect; chaos; coupled lattice maps.

1. Introduction

Different kinds of instabilities manifest in plastic flow experiments depending upon the mode of the experimental set up. Jerky flow or the Portevin-Le Chatelier effect (PLC) arises in a constant strain rate experiment. Although, this has been recognized as some kind of instability for a long time, it is only in the last decade that it has been analyzed from the point of dynamical systems. It has been long known that Jerky flow arises from the dynamic interaction of dislocations and mobile point defects and is referred to as dynamic strain ageing (DSA). It is this that induces a negative strain rate sensitivity (SRS) which in turn triggers the instability. Even so, several aspects of the phenomenon were not well understood until recently. In the past few years, there has been renewed attempts (Ananthakrishna and Sahoo 1981; Ananthakrishna and Valsakumar 1982; Valsakumar and Ananthakrishna 1983; Kubin and Estrin 1985, 1990; Zbib and Aifantis 1988; Jeanclaude and Fressengeas 1993; See also the papers in Viewpoint set 1993) to understand the phenomenon from the point of view of the theory of dynamical systems (Berge *et al* 1984; Hao Bai-lin 1988, 1989, 1990). The essential content of most of these studies is to re-examine all aspects of PLC in the light of the intrinsic nonlinear nature of the phenomenon. This has helped to get new insights hitherto not possible. All these theories emphasize the intrinsic nonlinearity inherent in the phenomenon. Of course, the details and levels of description of the phenomenon are different. One of the aims of such theories is to relate the microscopic dislocation mechanisms to the macroscopic measurable quantities. Even in such theories which stress the dynamical basis of the PLC effect, the negative SRS is an input in one form or

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the other with one notable exception of a model introduced by us. This attempts to derive all results as a consequence of the nonlinear interaction between the various types of dislocations (Ananthakrishna and Sahoo 1981; Ananthakrishna and Valsakumar 1982, 1983; Valsakumar and Ananthakrishna 1983; Ananthakrishna 1992a), including the negative SRS. For this reason, this model is completely dynamic in character. The method involves setting up the time evolution equations for the dislocation densities. The negative SRS results as a consequence of Hopf bifurcation from time homogeneous steady state to the time oscillatory state. Although, this theory ignored the spatial aspects, it proved to be surprisingly successful in that it could explain several features of the Jerky flow, such as the existence of a window of strain rates, temperature and solute concentration over which the phenomenon is seen, and the emergence of the negative SRS. One of the predictions of the model is that there is a range of values of applied strain rate where the plastic flow is chaotic (Ananthakrishna and Valsakumar 1983; Ananthakrishna 1990, 1992a). Recently, this prediction has been verified by analyzing the experimental signals from two distinct groups (Ananthakrishna 1992, 1994; Ananthakrishna 1993). It must be remembered that the experimental signals correspond to spatially extended system, and therefore, the existence of a strange attractor for the experimental signals with a fractal dimension d_f implies that $d = 2d_f + 1$ degrees of freedom correspond to collective degrees of freedom of the spatially extended system. This in turn means that the dynamical basis of the model viz. that there are only few dynamical degrees of freedom for the phenomenon is indeed correct.

One controversial aspect of the Jerky flow is devising an appropriate framework for including the spatial dependence (Kubin and Estrin 1985, 1990; Zbib and Aifantis 1988; Jeanclaude and Fressengeas 1993; Ananthakrishna 1993; See the papers in Viewpoint set 1993). There are several approaches which can be broadly classified as reaction-diffusion schemes. They largely depend on either long range dislocation interactions or the cross slip mechanism. In most cases, the negative SRS is an input into diffusion like equations (Zbib and Aifantis 1988; Jeanclaude and Fressengeas 1993; Kubin *et al* 1993). In contrast to these models, we have extended the above dynamical model by writing continuity equations which explain several features of the formation and propagation of the dislocation bands (Ananthakrishna 1993). The state of art of the subject is well summarized by the Viewpoint set of papers (Kubin *et al* 1993). Both these models are complicated in nature and hence not very transparent. The purpose of this paper is to present an alternate way to model the spatial aspects of the PLC effect on the basis of the predictions of both these dynamical models. One standard way to handle spatially extended dynamical system when individual elements are chaotic is to set up coupled lattice maps (Kaneko 1989). This will be done using the fact that the model predicts chaos and the one dimensional maps associated with the set of differential equations of the model are quadratic in nature (Feigenbaum 1978; Ananthakrishna and Valsakumar 1983; Ananthakrishna 1990, 1992a). We will attempt to provide arguments in support of such modelling. The plan of the paper is as follows. In § 2, we will very briefly recall the results relevant for building the coupled map lattice model. The model presented in §§ 3 and 4 contains results of the model. We end the paper by some remarks on the utility of such models.

In the following we will very briefly recall some relevant results of the model and make use of the results in setting up a coupled lattice map model. The dynamical model consists of three types of dislocations, viz. the mobile dislocations, the immobile dislocations, another type which may be regarded as dislocations with clouds of solute atoms (Ananthakrishna and Sahoo 1981; Ananthakrishna and Valsakumar 1982; Valsakumar and Ananthakrishna 1983). The corresponding densities are denoted by $\tilde{\rho}_m(t)$, $\tilde{\rho}_{im}(t)$ and $\tilde{\rho}_i(t)$ respectively. Using some well known dislocation mechanisms, we set up rate equations for the densities of the dislocations. Further details of the model can be found in the above references. These equations are then coupled to the machine equation for the rate of change of stress. There are several parameters in the model corresponding to the rate constants of the transformations. One parameter that must be mentioned is the exponent m which appears in the dependence of the velocity of dislocations on stress:

$$v(\sigma) = v_0 (\sigma/\sigma_0)^m,$$

where v_0 and σ_0 are constants. Another physically interesting drive parameter as a function of which the phenomenon occurs is the applied strain rate. There is a range of values of the parameters for which the steady state is unstable. Most of the analysis is carried out by keeping the parameter values within the instability domain and using the scaled strain rate e as the drive parameter. As e varied across the lower critical value, the behaviour changes from the normal yield to multiple yield. Simultaneously, we find that the negative SRS property sets in. The model also predicts an upper and a lower critical value for e and the scaled concentration of the solute atoms for the existence of the phenomenon. We shall refer to this model as a dynamical model (DM).

The above model exhibits chaos and has a rich variety of behaviour. There are several physically relevant variables such as the scaled strain rate, the velocity exponent, the concentration of solute atoms etc. Here, we summarize the chaotic behaviour exhibited by the model (Ananthakrishna and Valsakumar 1983; Ananthakrishna 1990, 1992a) when the strain rate is varied. The chaotic behaviour is seen in a window of intermediate values of the strain rates $\sim 10^{-4} \text{ sec}^{-1}$ (Ananthakrishna 1990, 1992a). A plot of the noisy sequence of ρ_m when the value of scaled strain rate $e = 184$ well inside the chaotic regime is shown in figure 1. It is clear that there is no detectable order and the plot looks completely random. However, this apparent randomness arises from a set of deterministic differential equations. In such a case, given the exact initial conditions, there is no uncertainty in predicting the future. However, given two orbits, even the smallest amount of indeterminacy in the initial conditions very soon explodes at an exponential rate rendering predictability of the future of the two orbits impossible. This sensitivity to initial conditions is a characteristic feature of chaotic systems and is quantified by Lyapunov exponent, which describes the rate of divergence of nearby orbits. There is an order in this chaotic behaviour which manifests in the form of self-similarity of the strange attractor in the phase space of the variables. Such a phase plot of ρ_m vs ρ_{im} showing a strange attractor is displayed in figure 2. Quantifying this self-similar structure distinguishes it from the stochastic noise

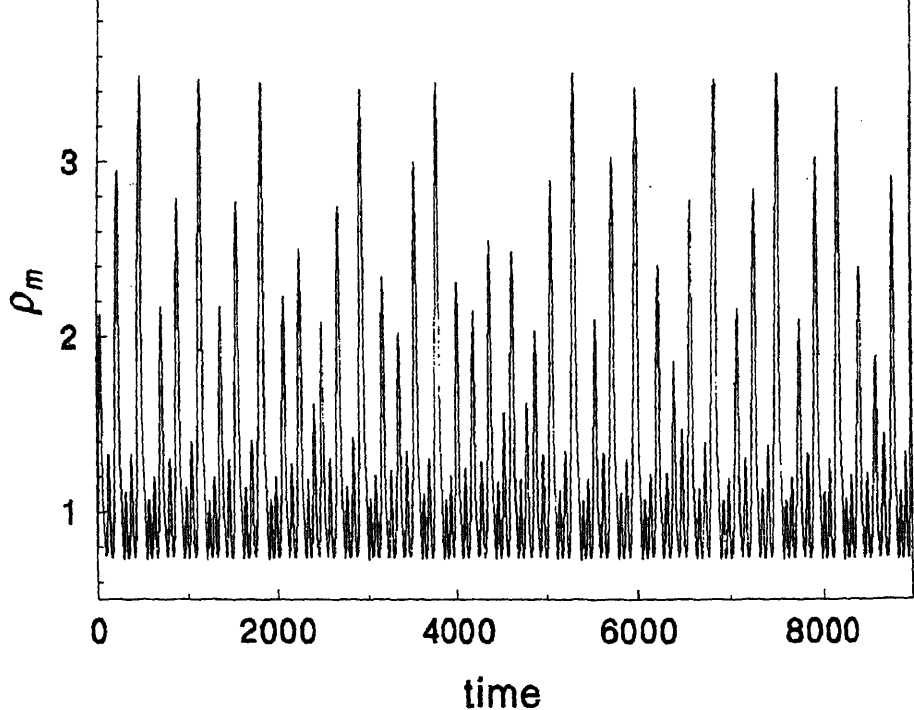


Figure 1. A chaotic plot of ρ_m as a function of time.

arising from many degrees of freedom. As a function of the applied strain rate, the model exhibits period doubling and period halving (backward) sequences. This rate of convergence of the period doubling sequence as a function of the drive parameter e , is measured by a quantity called Feigenbaum's exponent. When $m = 2$, we find the Feigenbaum exponent $\delta = 4.66$, which is the same as that for the one dimensional quadratic map (Feigenbaum 1978). This also means that the Poincare return map of this system has a quadratic maximum in all the four variables. One such map constructed by plotting $\phi(n+1)$ vs $\phi(n)$, where $\phi(n)$ is the peak value of the scaled stress at time n , is shown in figure 3. The nature of convergence of the period doubling and the period halving sequences is sensitive to the velocity exponent m . For instance, it exhibits a bubble structure for values of $m > 2$. The model predicts that the chaotic behaviour is seen only in a window of strain rates in which the PLC effect is observed. Since no experiment is free of noise inherent in the measuring instrument, one always finds that both types of signals are superposed on each other. There are a number of methods developed in the literature with varying degrees of sophistication which helps us distinguish the two different types of time series (Grassberger and Procaccia 1983; Wolf *et al* 1985; Broomhead and King 1986; Albano *et al* 1988). It is also possible to estimate the extent of stochastic noise superposed on the deterministic noise. Using one such method we were able to analyze two different sets of experimental signals.

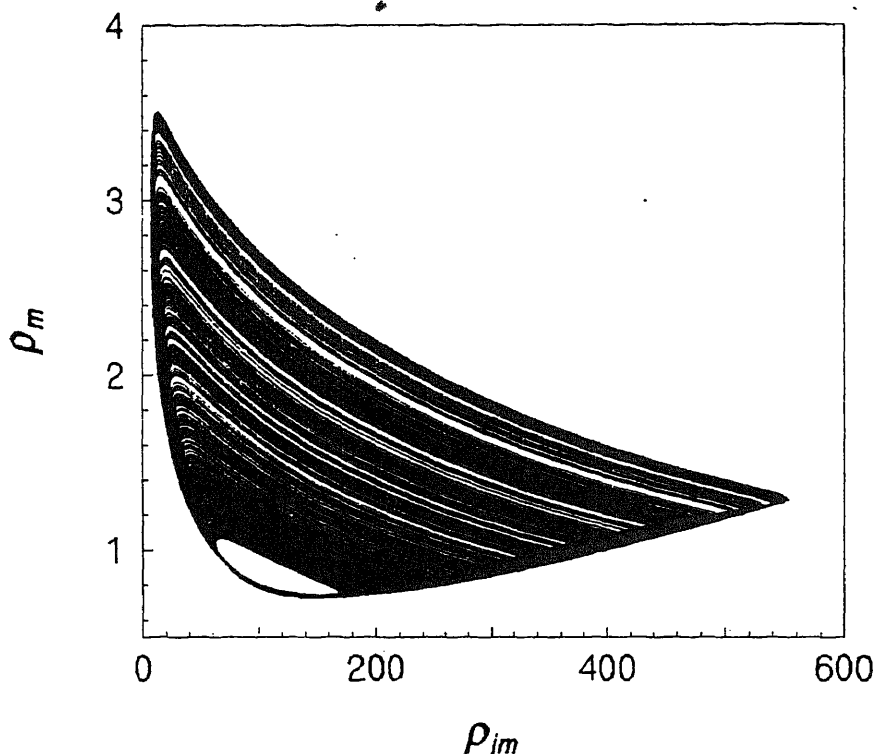


Figure 2. A phase plot of the scaled mobile dislocation density ρ_m vs the immobile dislocation density ρ_{im} , showing a self-similar structure.

The analysis showed that experimental signals of stress were indeed due to deterministic noise (Ananthakrishna *et al* 1992, 1994; Ananthakrishna 1993). This means that the prediction of the theory is correct. This also means that a correct description of the phenomenon should have a dynamical basis. In addition to this we could infer the following. As mentioned in the introduction the experimental sample is a spatially inhomogeneous and any spatially extended system has infinite degrees of freedom. Yet the signals show that the system behaves as if there are only a few degrees of freedom. Thus, these modes should correspond to collective degrees of freedom. We shall make use of this aspect in constructing a coupled lattice map for the description of the spatial aspect of jerky flow.

As mentioned in the introduction, devising an acceptable scheme for description of the formation and propagation of bands has been a controversial aspect. In spite of this, several models exist including our own attempt which involves extending the above model by introducing simple gradient terms for the dislocation densities. Thus, the starting point is just a set of continuity equations for the dislocation densities coupled to the machine equation which acts as a equation of constraint. For detail of this extended dynamical model (EDM) see Ananthakrishna (1993). Here we wish to emphasize that even with such a simple spatial term, EDM predicts the formation and propagation of dislocation bands. The velocity of the

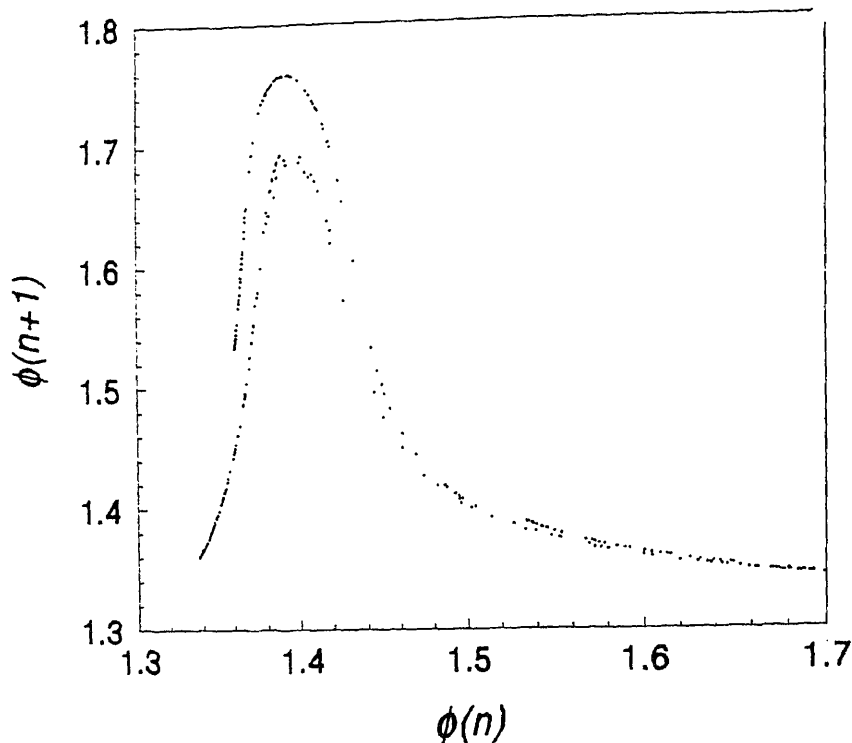


Figure 3. One dimensional map corresponding to the scaled stress ϕ .

band predicted by EDM is consistent with the only experimental measurement available in the literature (Chihab *et al* 1987).

3. A coupled map lattice model for the jerky flow

The method we follow here is to set up a coupled lattice map. Here one provides appropriate spatial coupling between the individual chaotic elements. In general such models are comparatively simple, yet they exhibit rich dynamics. In attempting to devise such a model, it would be desirable to preserve the basic features of the two models (DM and EDM). We will extract the pertinent points for devising a simple enough model compared to the two models summarized above. Such an attempt is certainly desirable, since the above models consist of coupled set of nonlinear differential equations and are difficult to analyze. We will use the following two aspects of DM and EDM. First, we will use the fact that all the four variables namely the three dislocation densities and the stress have a Poincare return map with a quadratic maximum. Second, we note that we introduced simple gradient terms into EDM as an additional feature. The first point implies that we could assume that each spatial element is behaving in a chaotic way. We further note that the quadratic nature of the Poincare maps of each of the variables is a result of nonlinear evolution equations. Second point implies that neighbouring elements

should be coupled using a first difference. Thus, to simplify the model even further we use just one dislocation density and the physically interesting density is the mobile dislocation density. (This limits the extent to which we can interpret the results as we will see later.) We note further that the values of the variables we encounter in the one dimensional maps are restricted to the domain $[0, 1]$. Thus, all the variables in the coupled lattice model corresponding to the old variables should be scaled appropriately so that their values are in this domain. We shall denote the corresponding density by $x(n, i)$, where n refers to the time index and i refers to the spatial position on a one dimensional lattice. Recall that in EDM, we have a term $\nabla(v(\sigma)p_m)$, in the continuity equation for the mobile density. Here the velocity of dislocations are functions of the applied stress σ . This will be function of time alone. We will denote the scaled stress by $\phi(n)$. We further recall that the phenomenon occurs as a function of the drive parameter, namely, the applied strain rate and this parameter appears in the stress equation only. This means that the parameter that we will introduce the map for $\phi(n)$ should be taken to correspond to the applied strain rate scaled appropriately, which we will denote by s (in such a way that its range is from 0 to 4). With these observations, we can write down the simplest form of a coupled lattice map as follows.

$$x(n, i) = prf(x(n, i)) + (1 - p) [s\phi(n)]^2 [f(x(n, i - 1)) - f(x(n, i))], \quad (1)$$

$$\phi(n + 1) = sf(\phi(n)), \quad (2)$$

$$f(y) = y[1 - y]. \quad (3)$$

The velocity of dislocations as stated earlier is some power of the stress. For this reason we have introduced the term $[s\phi(n)]^2$ as a multiplicative term in the gradient of $x(n, i)$. Note that the exponent used then corresponds to $m = 2$. (Recall that it is for this case that we get a quadratic Poincare map.) The parameter r is a control parameter for the quadratic map corresponding to $x(n, i)$. From DM we know that r should be a function of applied strain rate apart from other parameters. Since we do not know the exact dependence, we will introduce it as a tuning parameter as a function of which the period doubling bifurcation arises. It is conventional to introduce an additional parameter p to signify the on-site strength and $(1 - p)$ to the near neighbour coupling (Kaneko 1989).

4. Results and discussion

The time evolution of the system is studied by preparing the system with random initial conditions for $x(0, i)$ and nonzero but small value for $\phi(0)$. We impose periodic boundary conditions on the lattice. For most part of our computations we have used a lattice size of 200 points. The values of the parameters used are $r = s = 3.8$ and $p = 0.1$. This means that the on-site term gives period two (because, $r \cdot p = 3.42$ which falls in the domain of period two) for the dislocation density, but keeps the stress in the chaotic zone. In a short time, a very heterogeneous structure develops, with high and low value for the dislocation density as a function of spatial position. A typical early configuration for $n = 60$ is shown in figure 4a. Figures 4b–e show the configurations at various times. As time progresses, we

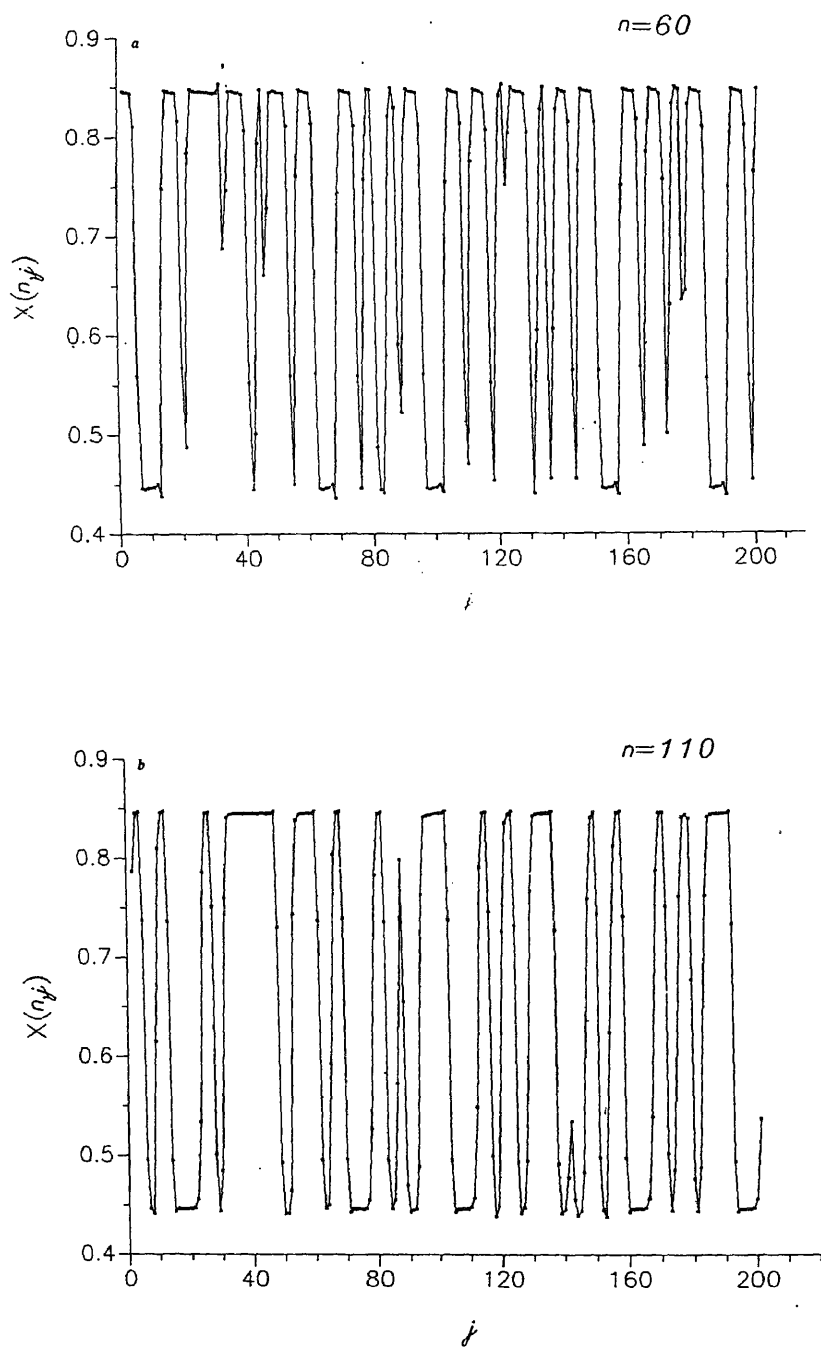


Figure 4a-b. For caption, see p. 780.

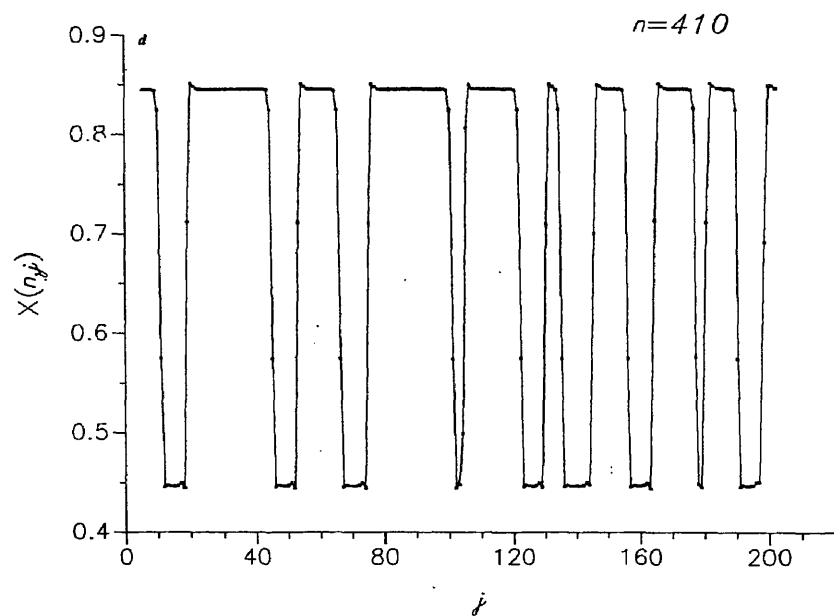
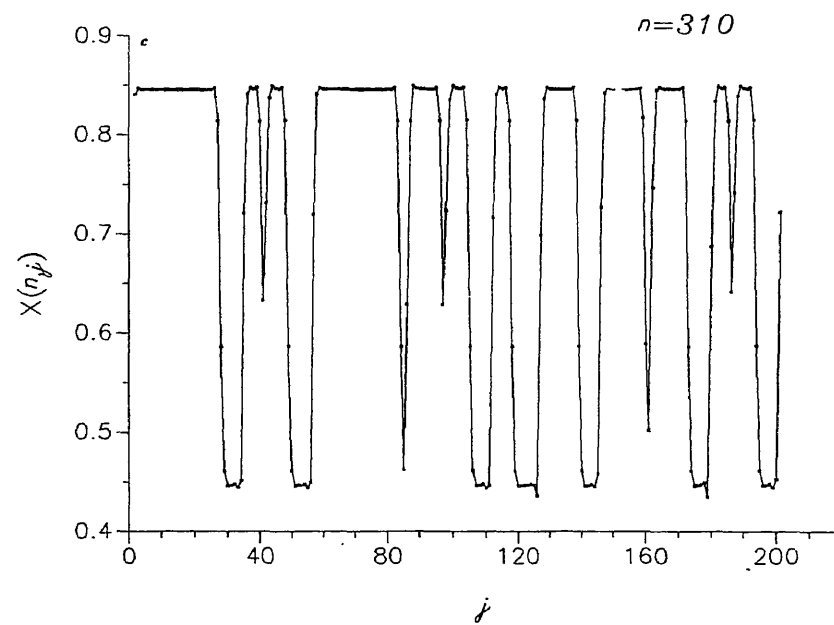


Figure 4c-d. For caption, see p. 780.

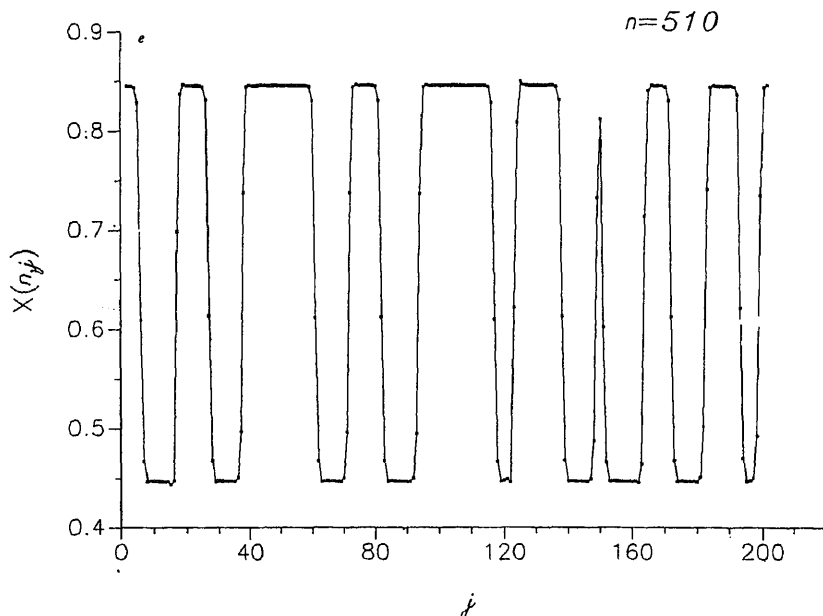


Figure 4. a. Dislocation density at various spatial points at an early stage of simulation ($n = 60$), b. dislocation density at various spatial points at a fairly early stage of simulation ($n = 110$), c. dislocation density at various spatial points at an intermediate time ($n = 310$), d. dislocation density at various spatial points at a late stage ($n = 410$) and e. dislocation density at various spatial points at a late stage ($n = 510$).

generally see two types of changes. In the early part of the simulation, we see that the width of the local bands with high and low dislocation densities are generally increasing. This can be seen by comparing the configuration of $n = 60$ with $n = 110$. We see that the bands with high and low dislocation densities have expanded by suppressing the rapid fluctuations. This is what one would expect physically in a realistic situation also. Second feature is that at later stages we see that in general the bands with high dislocation densities are expanding into the regions of low dislocation density. This can be seen by comparing the configurations at $n = 410$ and $n = 510$. Again, one should expect that this general feature is correct, since if we regard that low mobile dislocation density corresponds to no other type of dislocations, this would amount to less strain and one should expect that the front of the dislocation bands move into a region of lower strain. It must be remarked here that this is a consequence of the simplicity of the model, since, it is possible that low mobile dislocation density could correspond to high immobile or forest dislocations. At later stages, for example, an attempt to overlay the configurations with most parts overlapping (some will not, for reasons that will be stated below), shows that the system as a whole 'moves' forward. For instance, if the first broad band of high x value from $i = 20$ to 42 at time $n = 410$, is taken to correspond to the first broad band at $i = 40$ at a time $n = 510$, we see that the system as a whole appears to 'move' forward. (Note that the sites from 480

onward at $n = 410$ then correspond to the sites from 0 to 20 due to the periodic boundary conditions.) Although, this might give the impression of new bands being created at the grips which once again pass into the sample, one does not know if this can be taken as a proper interpretation. One other aspect that need to be studied is the effect of the chaotic behaviour of the stress equation. In principle, it should induce newer and newer pulses in to the spatial part. This should induce new bands created at random. We have not examined this aspect in detail. It must be remarked here that we have presented the simplest coupled lattice model. It is possible to develop more realistic models. Further work and perhaps evolving better coupled lattice map models are worth examining. Such attempts are in progress.

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Average lattices and aperiodic structures

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Abstract. Statistically averaged lattices provide a common basis to understand the diffraction properties of structures displaying deviations from regular crystal structures. An average lattice is defined and examples are given in one and two dimensions along with their diffraction patterns. The absence of periodicity in reciprocal space corresponding to aperiodic structures is shown to arise out of different projected spacings that are irrationally related, when the grid points are projected along the chosen coordinate axes. It is shown that the projected length scales are important factors which determine the existence or absence of observable periodicity in the diffraction pattern more than the sequence of arrangement.

Keywords. Lattice; diffraction; incommensurate; quasicrystals.

1. Introduction

Deviations from strictly periodic and crystallographically allowed symmetries are known and they are commonly referred to as aperiodic structures. The incommensurate phases are aperiodic structures with crystallographically allowed rotational symmetries (Fujiwara 1957; Hirabayashi and Ogawa 1957; Sato and Toth 1961, 1962; McMillan 1976; de Wolff 1977; Amelinckx 1979; Cowley 1979; de Wolff *et al* 1981; Perez-Mato *et al* 1987; Quan *et al* 1987; Simmons and Heine 1987). The quasicrystals are examples of aperiodic structures with crystallographically disallowed rotational symmetries (Shechtman *et al* 1984; Steinhardt and Ostlund 1987). It is desirable to examine whether the different aperiodic structures can be brought under the same frame work in relation to their diffraction properties keeping in mind that an approach that suits diffraction properties might not be suitable for other manifestations like shape or other physical properties. The characteristic feature of incommensurate crystals is the presence of superlattice reflections in their diffraction patterns and that of quasicrystals is their unusual rotational symmetry in addition to the quasiperiodic spacings of reflections. In the present work, focus will be on the role of the numerical length scales forming the spacings in real space, in conjunction with the sequence of arrangement of these spacings in determining these characteristic features. Examples in one and two dimensions to illustrate the importance of length scales are provided.

2. Definition of an average lattice

The concept of an average lattice is best illustrated with an example. Figure 1 shows a grid constructed by two orthogonal vectors. The magnitude of the vectors along X and Y directions are 1.0 and 0.25 respectively. The lattice points are the

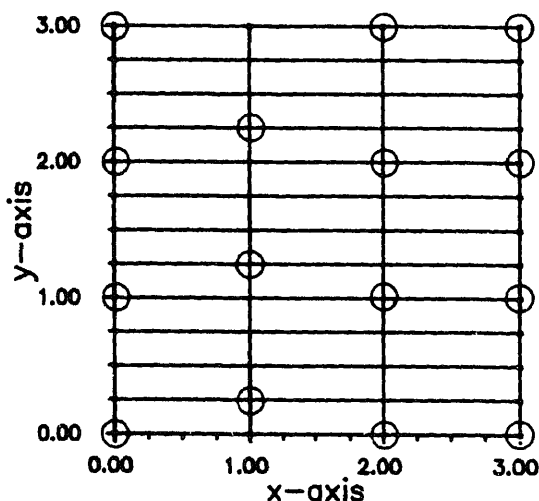


Figure 1. A grid and some scatterers. Partial occupancy of a grid leads to the definition of an average lattice.

grid intersections. The lattice points that are occupied by scatterers are marked by circles. Since the scatterers will be atoms, there exists a minimum separation between them. However, there is no such restriction on grid points. Therefore, in principle, the grid points could be arbitrarily close. However, when a chosen lattice point is occupied, it prevents any other lattice point that is within a certain radius from being occupied. This results in a situation in which the lattice contains a partial occupancy of scatterers. For the present discussion it is necessary to distinguish unoccupied lattice points from vacancies. The unoccupied lattice sites are disallowed sites. Allowed sites which remain unoccupied for other reasons are called vacancies. Note that there are several ways in which the fifteen scatterers shown in figure 1 can be redistributed over the lattice. We will soon see that the major features of a diffraction pattern are dictated by the full lattice and minor features arise out of the nature of the distribution of the scatterers.

In order to show that a distribution as shown in figure 1 is realistic, let us consider the example shown in figure 2a. This figure is a regular square lattice in two dimensions with unit lattice spacing. Suppose one applies a modulation of a type governed by the following set of equations:

$$y = \begin{cases} 0.25 & \text{if } \cos wx \geq 0; \\ 0, & \text{otherwise.} \end{cases} \quad (1)$$

The equation implies that when the modulation wave travels along the X-axis, the scatterers get displaced along the Y-axis. Figure 2b illustrates the result of applying the modulation to figure 2a. Some scatterers are displaced by a quantity 0.25 which is the amplitude of modulation. The modulation wavelength is taken to be very large compared to the size of the figure and this leads to an aperiodic modulation within the figure. Actually figure 1 is a subset of figure 2b. Owing to

the modulation, the square lattice has transformed into a dense grid with partial occupancy. One can calculate the diffraction pattern of figure 2b by computing the Patterson function assuming unit delta function scatterers at the occupied sites. The diffraction pattern for the set of scatterers in figure 2b is shown in figure 2c. It is seen that the periodicity of reflection with unit spacings along X^* direction

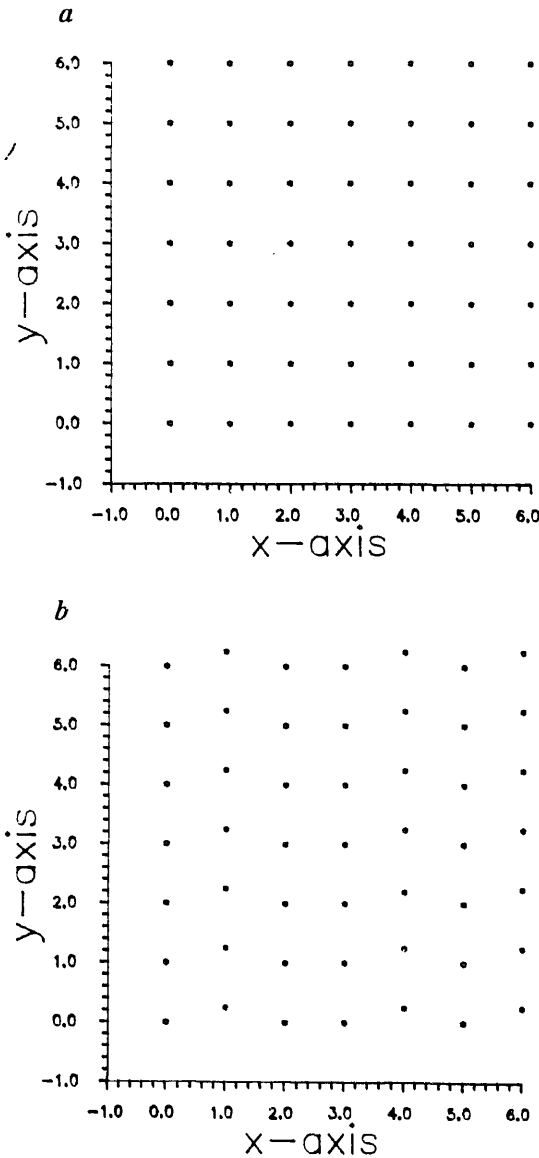


Figure 2a-b. For caption, see p. 786.

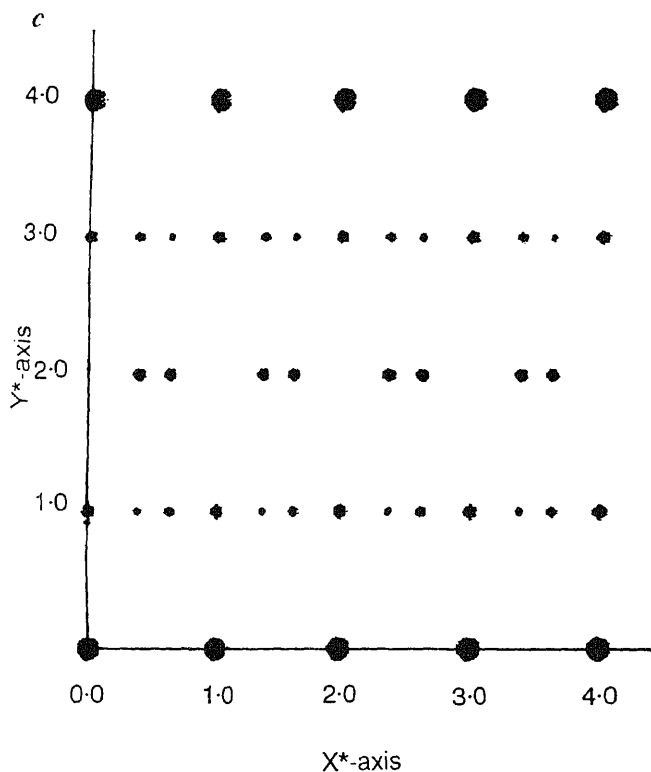


Figure 2. a. Periodic lattice, b. modulation wave along X and modulation along Y (modulation amplitude is rational) and c. diffraction pattern for the distribution of scatterers shown in b.

remains unaffected with respect to what one would obtain without modulation. However, the diffraction pattern is significantly changed along the Y^* direction. The periodicity along Y^* is now 4 units. There is a reciprocal space unit cell of 1×4 . Note that it is necessary to consider both the intensity and position of the reflections to define a reciprocal space unit cell (an analogy to real space unit cell which is defined over the translation with respect to the same type of scatterer). The reciprocal space unit cell size is 1×4 owing to the real space unit cell of 1×0.25 (not drawn on figure 2b). If all the vertices of the grid (spanned by 1×0.25 in figure 2b) were occupied, then we would not obtain the reflections which occur within the 1×4 cell in the reciprocal space. The inner reflections within the 1×4 cell occur with a periodicity inversely proportional to the modulation wavelength. There are weak satellite reflections by the side of strong reflections which are not observable from the figure, but can be readily obtained from the Patterson.

Let us consider a more general example. Figure 3a shows the result of modulation in figure 2a, applied along X and Y directions. It is seen from the figure that there is no apparent periodicity in the distribution of scatterers. However, the diffraction pattern shown in figure 3b brings out aperiodicity. There is a clear set of reflections within a cell of 4×4 unit square which repeats itself in the reciprocal

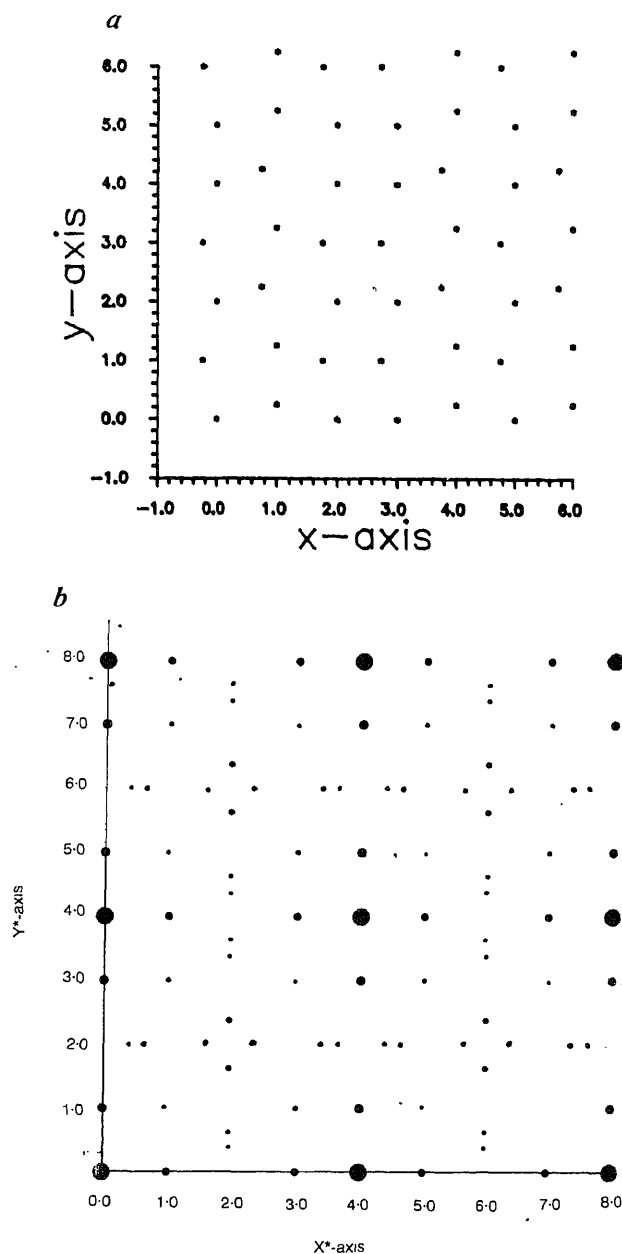


Figure 3. **a.** An aperiodic distribution of scatterers obtained by modulating a periodic distribution gives a partially occupied dense lattice and **b.** periodic diffraction from 3a.

space. This is a classic example, in which the distribution of scatterers do not appear to possess aperiodic order while its diffraction pattern is periodic. In fact, figure 3b is similar to the diffraction pattern observed for incommensurate phases. In the conventional notion of incommensurate structures, the periodic set of strong reflections are usually considered as main reflections and the weak inner reflections

are considered to be superlattice reflections. The physical structure is supposed to be composed of two types of occupants, one being a periodically fixed set of scatterers (leading to the main reflections) and the other following a displacive modulation (leading to the superlattice reflections). However, we find that there is no need for a fixed set of scatterers. The distribution of scatterers in figure 3a formed a set of partially filled dense lattice whose basis vectors determined the reciprocal lattice. We are thus in a position to define an average lattice as a regular compact lattice with a distribution of disallowed sites. The term average gains importance from the fact that this distribution can be often unpredictable.

3. One dimensional average lattices

The effect of partial occupancy of a lattice can be better understood if one studies the following one dimensional example. Figure 4a shows a large unit cell structure in which there are three scatterers within a unit cell of 1 unit. For the sake of simplicity, it is assumed that these scatterers are located at 0.25, 0.5, 0.75, 1.25, 1.5 etc with positions 0, 1, 2 etc as unoccupied. One can readily calculate the diffraction pattern for such a distribution of scatterers by evaluating the structure factor given by

$$S(h) = \exp(-2\pi i h * 0.25) + \exp(-2\pi i h * 0.5) + \exp(-2\pi i h * 0.75). \quad (2)$$

The $S(h)$ values for h -values 0 to 4 will be 3, 1, 1, 1, 3 and these values will repeat for other integral values of h . Alternatively one can calculate the same diffraction pattern by considering the distribution of scatterers (figure 4a) as a difference of two simple lattices constructed by vectors 1 and 4 respectively (as shown in figure 4b). The structure factor of the simple lattice ($a = 0.25$) is given by

$$S(h') = 1 + \exp(-2\pi i h') + \exp(-4\pi i h') + \exp(-6\pi i h'). \quad (3)$$

The structure factor of the other simple lattice ($a = 1$) is given by

$$S(h'') = 1. \quad (4)$$

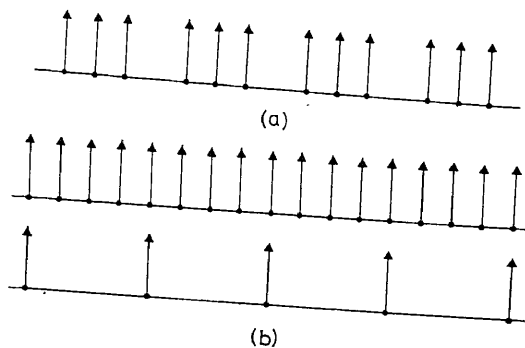


Figure 4. a. A large unit cell with 3 scatterers and b. the large unit cell as a difference lattice of two simple lattices with periodicities 1 and 4.

Equation (2) is obtained by subtracting (4) from (3) realizing that $h = 4h'$.

In this example it turned out that the unoccupied sites are periodic and therefore the resultant distribution formed a regular periodic structure. However, if the unoccupied sites are not periodic, the resultant structure forms an average lattice structure. The distribution of scatterers in figure 5a is random (with spacings 1.6 and 1). The diffraction pattern for this distribution is shown in figure 5b. It is clearly seen that the reciprocal space periodicity (RSP) of 5 units is inversely proportional to the highest common factor (0.2) between the two length scales forming the sequence. This shows that there is a one-dimensional lattice ($a = 0.2$) which is partially occupied and the reciprocal space unit cell has been determined by this lattice.

In order to show that the RSP is dependent on the commensuration of two spacings, another example is shown in figure 5c. The two spacings are rationally related (spacings 1.6 and 1) and the sequence of arrangement is the Fibonacci sequence. Figure 5d demonstrates the RSP of 5 units in the reciprocal space. This is again another classic example in which it can be seen that the Fibonacci sequence can lead to a periodic diffraction. Therefore the sequence of arrangement of the length scales is not a sufficient condition for an aperiodic diffraction. The ratio of length scales forming the two spacings are the important factors which determine a unit cell in reciprocal space. Let us consider the other extreme example in which the length scales are irrationally related (spacings are the golden mean τ and 1) but the sequence of arrangement is periodic. One can readily evaluate the structure factor at intervals of $1/(1+\tau)$. The intensities of expected reflections are listed in table 1. From table 1 one finds that there is no periodicity in the reciprocal space if one considers both position and intensity of reflections. The positions of strong reflections follow the Fibonacci sequence (1, 2, 3, 5, 8). Owing to the irrationality between the two spacings, the actual grid has become infinitely dense and this leads to an RSP of infinity.

4. Incommensurate phases and quasicrystals

The diffraction pattern from modulated structures arise out of two factors. The first factor is associated with the amplitude of modulation of the scatterers from a mean position. The second factor is the wavelength modulating wave. The strong periodic reflections occur owing to the amplitude of modulation. The weak inner reflections occur with a periodicity inversely proportional to the wavelength of the modulating wave. The incommensurate phases have rational amplitude of modulation and a large modulation wavelength. If the modulation is periodic and travels along any axial direction then all the reflections from the modulated structure can be readily calculated. Since the modulation need not be along any axial direction, the length scales forming the sequence and the sequence itself could be aperiodic. Figure 6a shows a typical situation in two dimensions. The spacings of projected length scales are aperiodic (related by the golden mean and the sequence is Fibonacci). Figure 6b shows the calculated diffraction pattern. The positions of the reflections are not periodic and related by the golden mean. The intensities also scale up by the Fibonacci sequence. This example illustrates that a diffraction pattern could arise simply by a periodic or an aperiodic distribution of a finite number of length scales.

Regular body centred cubic structures in some alloys possess local icosahedral clusters. Let us consider a typical crystal structure in which undistorted icosahedra are sharing vertices. Every vertex in such a structure is obtainable by a linear combination of the six icosahedral vectors. From such a distribution of vertices it is possible to extract a subset of vertices, which in turn, satisfies the conditions to form a quasicrystal. This can be symbolically represented as,

$$S_{\text{actual}} = S_{\text{crystal}} \cap S_{\text{quasiperiodic}} \quad (5)$$

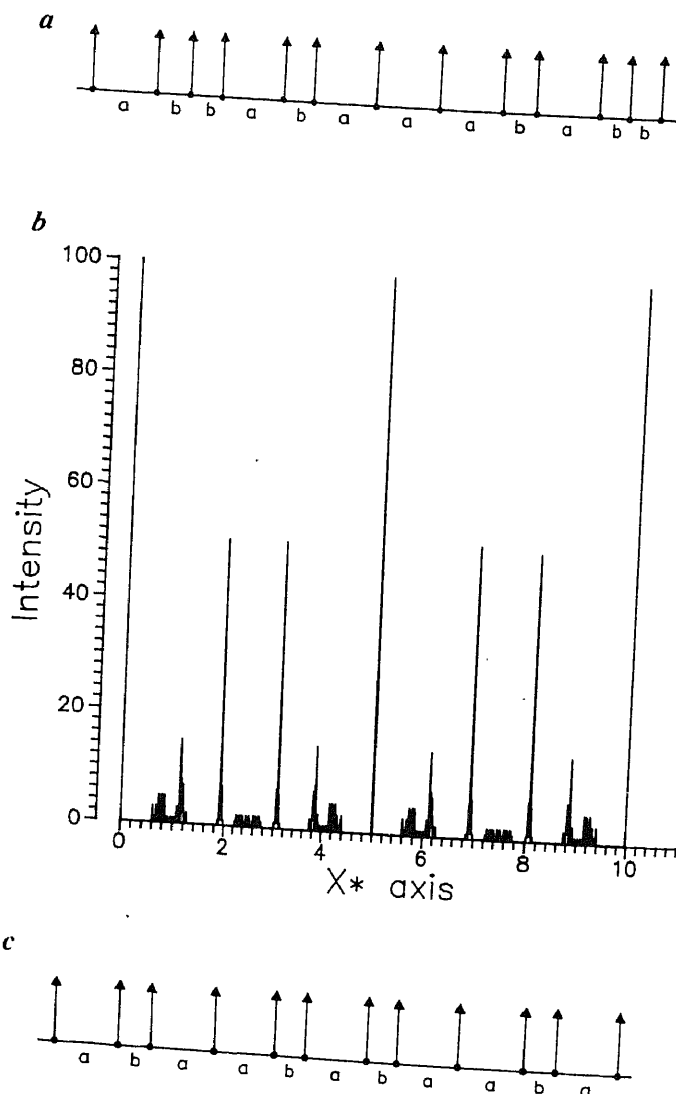


Figure 5a-c. For caption, see p 791.

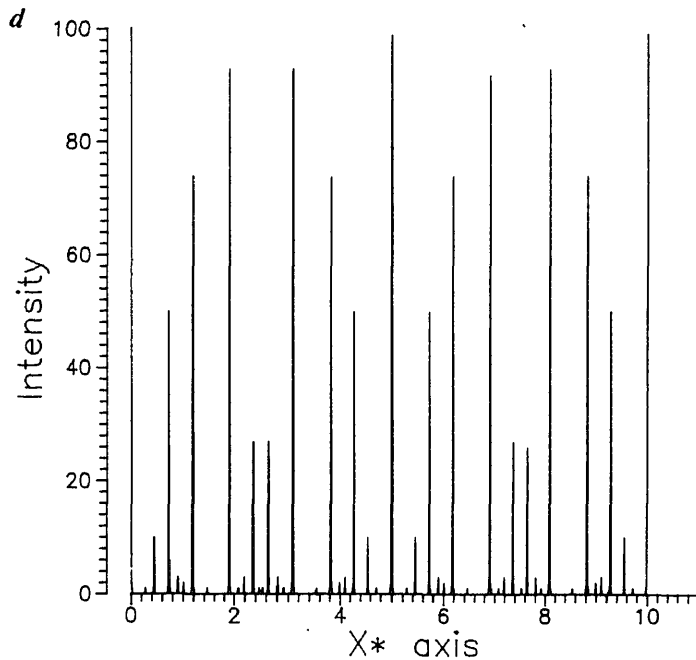


Figure 5. Two length scale average lattices in one dimension and their diffraction patterns: **a.** $a : b = 1.6 : 1$ and the sequence is random, **b.** diffraction pattern that brings out the hidden periodicity in **a**, **c.** $a : b = 1.6 : 1$ and the sequence is Fibonacci and **d.** a periodic diffraction pattern from **c**. Note the periodicity of reflections at intervals of 5 units in both **b** and **d**.

Table 1. The calculated diffraction pattern for a periodic distribution with two spacings 1 and τ .

Position	Intensity	h -value	Position	Intensity	h -value
0.0	100	0	7.639	17	20
0.382	13	1	8.021	99	21
0.764	54	2	8.403	8	22
1.146	80	3	8.785	60	23
1.528	0	4	9.167	74	24
1.91	92	5	9.549	2	25
2.292	37	6	9.931	95	26
2.674	26	7	10.313	30	27
3.056	96	8	10.695	33	28
3.438	3	9	11.077	94	29
3.82	71	10	11.459	1	30
4.202	64	11	11.841	77	31
4.584	6	12	12.223	58	32
4.966	98	13	12.605	10	33
5.348	21	14	12.987	99	34
5.729	43	15	13.369	16	35
6.111	88	16	13.751	50	36
6.493	0	17	14.133	83	37
6.875	85	18	14.515	0	38
7.257	47	19	14.897	89	39

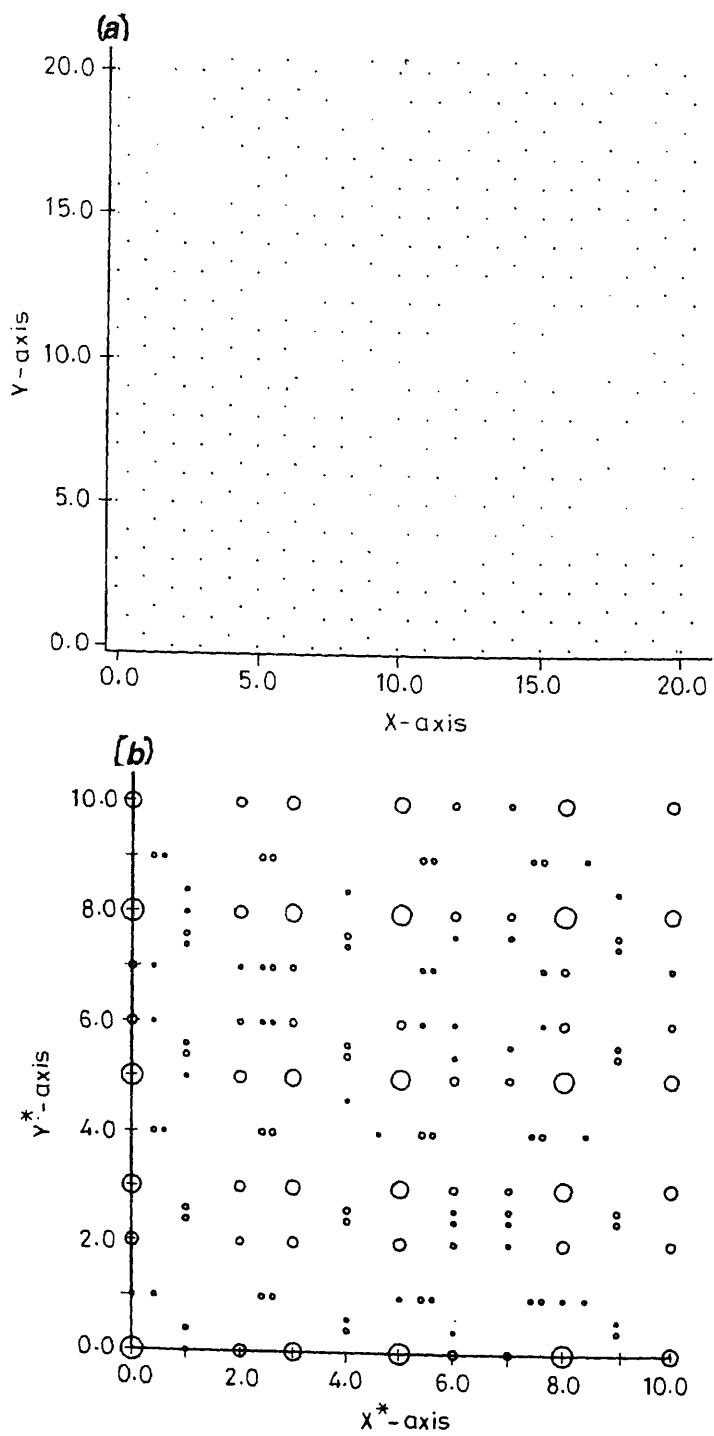


Figure 6. a. Two dimensional distribution of scatterers with irrational spacings and aperiodic modulation and b. diffraction pattern for the distribution in a. Observe that the spacings and the intensities follow the Fibonacci sequence.

The intersection of two sets, one being a collection of vertices in a crystal structure and the other forming a quasiperiodic set, may not be a dense space filling set. Nevertheless, it is seen that one does not require displacement of scatterers from a normal crystal structure to form a quasicrystalline distribution. Accordingly a quasicrystal can result as a special collection of incomplete icosahedra from its parent crystal structure without displacing scatterers. Since the icosahedra could also be sharing faces (instead of sharing edges) in the parent crystal structure, the quasicrystalline structure extracted from it will be different. In this context, it is important to point out that a regular simple cubic structure with two icosahedra per unit cell (sharing three vertices along the $\langle 111 \rangle$ direction) can provide a better starting model for extracting a quasicrystalline type structure. This will be discussed in due course.

Conclusions

We have presented a different perspective to the problem of aperiodicity in materials, mainly with their diffraction pattern in consideration. Modulations lead to the observed diffraction pattern for incommensurate phases when the modulation amplitude has a rational intercept. Partial occupancy of a crystal structure with local icosahedral symmetry leads to structures analogous to quasicrystalline structures. Since the disallowed sites form a quasiperiodic distribution they are directly related to the vacancy ordered phases (Chattopadhyay *et al* 1987). However, the vacancies are treated as disallowed sites in the present context. This is necessary to obtain the results for the incommensurate phases. The addition of phases in Fourier transform required for diffraction occurs owing to the relationship between different length scales in the distribution of scatterers. The examples considered here may be useful for a careful evaluation of structures that appear to be quasicrystalline (Baranidharan 1993).

Acknowledgements

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An electron diffraction study of quasicrystals in Ti-37 at% Mn and Ti-24 at% Mn-13 at% Fe alloys

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Abstract. Electron diffraction studies were carried out to establish the icosahedral phase formation in rapidly quenched Ti-37 at% Mn and Ti-24 at% Mn-13 at% Fe alloys. Distortions in the diffraction spots and diffuse intensities in the diffraction patterns were investigated. The existence of a rational approximant structure and a decagonal like phase are also reported.

Keywords. Quasicrystals; electron diffraction; titanium alloys.

1. Introduction

A remarkable discovery was made in the year 1984 by Shechtman *et al* (1984) while studying the electron diffraction patterns of rapidly quenched Al-Mn alloys when they reported the formation of a solid phase, 1–2 μm in size, giving rise to sharp diffraction intensities like a single crystal but with a point group symmetry $m\bar{3}5$ which is inconsistent with lattice translations.

The basic principles governing the synthesis of the quasicrystals can be simply understood as being based on the following criteria: (i) icosahedral crystal structure criterion, which derives its basis on the existence of crystalline phases possessing short range icosahedral order (Ramachandra Rao and Sastry 1985; Henley and Elser 1986), (ii) quantum structural diagram criterion based on quantum properties of the elements, and (iii) the phase diagram criterion—where a peritectic reaction is featured by the quasicrystal forming alloys.

While there are isolated examples of quasicrystals based on Pd and Li alloys, the vast majority of quasicrystals are aluminium-, magnesium- and titanium-based alloys (Ranganathan and Chattopadhyay 1991). Titanium based quasicrystals are attracting increasing attention, since their original discovery by Zhang *et al* (1985). Bhaskaran (1992) and Kelton (1994) have reviewed titanium quasicrystals as well as closely related rational approximant structures.

The occurrence of quasicrystals in Ti-Mn system is quite interesting since it does not follow any of the criteria discussed above (Kelton *et al* 1988). The Ti-Mn phase diagram does not show the Ti_2Mn phase. The reported composition of I-phase in Ti-Mn alloy is near eutectic composition which is 37 at% Mn. Kelton (1994) has shown the existence of higher order crystalline approximant structures in these alloys. From a comparison of the various models he pointed out the near agreement of the experimental results on arcs of diffuse intensity with the icosahedral glass model.

X-ray diffraction (XRD) studies on the rapidly quenched Ti-Mn alloys (Yavari

and Verger-Gaugry 1988) showed close similarities to the icosahedral phase suggesting that its formation may be possible in this system. Kelton and co-workers (1988) were the first to successfully synthesize icosahedral quasicrystals in Ti-Mn alloys. The I-phase in Ti-Mn alloys assumes more significance because of the occurrence of arcs of diffuse scattering in electron diffraction patterns. It is believed that the position and intensity of these arcs will give valuable information about the atomic decoration (occupancy) of the quasicrystal lattice (Gibbons *et al* 1989). The stability of the quasicrystal in this alloy has been studied by Holzer *et al* (1989). It has been reported that the I-phase is stable below 1075 K. Annealing at 1130 K for 30 min resulted in complete transformation of the I-phase. The transformation products did not correspond to any of the equilibrium phases. Further, a cubic phase with $a = 13.44 \text{ \AA}$ corresponding to the 1/1 approximant structure has been found to occur (Kelton 1989).

In this paper the I-phase formation in rapidly quenched Ti-37 at% Mn alloy and the occurrence of diffuse intensity are discussed. Transmission electron microscopy (TEM) studies were carried out to compare the characteristics of the quasicrystalline phase in this alloy to those of Al and Mg base quasicrystals and to determine whether any other competing phases are present. XRD has been used to characterize melt spun ribbons of this material and the vertex vectors of the I-phase determined for calculation of the quasilattice constant. TEM in conjunction with selected area electron diffraction (SAED) techniques have also been employed. A possible rational approximant structure closely connected to the I-phase has been identified. In addition, the shape distortion of the diffraction spots is reported. An icosahedral quasicrystal has also been observed in the rapidly quenched Ti-24 at% Mn-13 at% Fe alloy. The alloys used in this study have a silicon content of 2 to 3 at%. It appears that the presence of silicon is essential for the formation of I-phase in these alloys (Kelton *et al* 1988).

2. Experimental

The melt spun ribbons of Ti-37 at% Mn and Ti-24 at% Mn-13 at% Fe were provided by Kelton. The details of melt spinning are given elsewhere (Kelton *et al* 1988). The ribbons were annealed in vacuum at 573 and 873 K respectively for 15 min. Thin foils for electron microscopy were prepared in a Tenupol twin jet electropolishing unit using an electrolyte of 90% methanol and 10% sulphuric acid at 223 K and under a d.c. potential of 30 V. Some samples were also prepared by ion thinning. The thin foils were observed in a Philips EM 300 and JEOL-200CX TEM operating at 100 and 200 kV respectively. XRD was carried out in a Philips X-ray diffractometer using copper K_{α} radiation at 40 kV.

3. Results and discussion

3.1 Quasicrystals in titanium-37 at% manganese alloy

3.1a Electron diffraction and microscopy: The XRD data of the as rapidly quenched alloy are given in table 1. The indexing has been carried out according to Bancel *et al* (1985). The co-existence of the I-phase with other metastable phases is

Table 1. X-ray diffraction results of rapidly quenched Ti-37 at% Mn alloy.

2 θ	d (Å)	Intensity	Phase	Index
35.8	2.501	w	I	(21 $\bar{1}$ 001)
39.8	2.264	m	TiMn; β Ti(Mn)	(320); (110)
40.4	2.232	s	I	(100000)
40.8	2.211	m	TiMn	(313)
41.6	2.170	m	TiMn	(205)
42.5	2.126	m	I	(110000)
43.45	2.082	mw	I	(220002)
58.5	1.577	w	β -Ti(Mn)	(200)
71.8	1.314	w	I	(2110 $\bar{1}$ 1)
72.2	1.308	w	β -Ti(Mn)	(211)
73.35	1.290	w	I	(101000)

w, weak; mw, medium weak; m, medium; s, strong.

indicated by the X-ray data. The competing crystalline phases are the β -Ti (Mn) and TiMn. It is observed that the vertex vector (100000) is stronger than the edge vector (110000). This is also the case in Al-Mn alloys reported by Bancel *et al* (1985). However, the intensities are reversed in Mg-based quasicrystals (Mukhopadhyay 1989).

TEM studies revealed that a wide variation in the size of quasicrystals ranging from 0.07 μ m to 0.5 μ m exists. From figure 1 it is seen that the coarser quasicrystals co-exist with the β titanium at the rim of the quasicrystals. The quasicrystals exhibit very fine dendritic morphology and speckle contrast with each quasicrystal divided into a number of sectors. It was found that electron diffraction ring patterns obtained from the area containing very fine grains could be indexed in terms of the I-phase. The d spacings of the rings in the electron diffraction pattern are in the τ ratio of 1.618.

Figures 2a-c are SAED patterns taken with the electron beam parallel to the $\bar{1}$ -fold, 3-fold and $\bar{2}$ -fold axis directions, respectively, in the quasicrystalline phase, confirming the $m\bar{3}\bar{5}$ symmetry. In addition the $[\bar{1}10]$ zone axis pattern was also obtained (figure 2d). Dark field image of the quasicrystal showed that the entire quasicrystal is illuminated suggesting that all the sectors inside the quasicrystal possess the same orientation.

The variation in the size of the quasicrystal observed is in accordance with the study of Kelton *et al* (1988). The internal structure of the quasicrystal is very similar to that of the I-phase reported in $\text{Mg}_{32}(\text{Al-Zn-Cu})_{48}$ and in many other Al-Mn alloys (Mukhopadhyay *et al* 1987a). However, in the present case the boundaries between the quasicrystals are not faceted. Instead, they are irregular (figure 1). The speckle contrast observed can be interpreted on the basis of the results of Knowles and Stobbs (1987) who carried out detailed dark field imaging of the quasicrystals to understand the origin of the speckle contrast and traced it to the chemical inhomogeneities present in the quasicrystalline phase. It has been pointed out by Kim *et al* (1990) that various factors such as micrograin structure, topological defects like phasons and phonons, chemical inhomogeneity, local periodicity and decagonal phase may be sources for the observed deviations from the icosahedral symmetry.

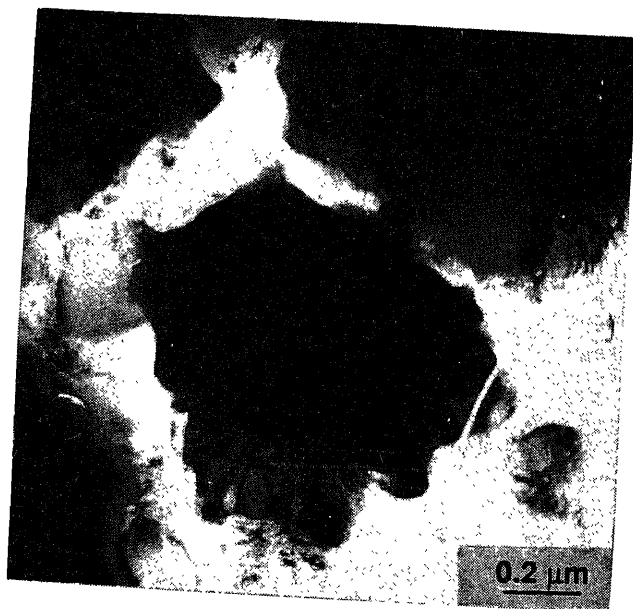


Figure 1. TEM of melt spun Ti-37% Mn alloy showing icosahedral quasicrystals exhibiting speckle contrast with retained β surrounding the rim of the I-phase.

3.1b Quasilattice constant: The quasilattice constant has been defined as the edge length (a_R) of the rhombohedra of the three dimensional Penrose tiling (Elser and Henley 1985). The quasilattice constant is calculated as

$$a_R = (\tau^3/2) \cdot d_{100000}.$$

Substituting the value of $d_{100000} = 2.232 \text{ \AA}$ in the above expression the quasilattice constant (a_R) is equal to $4.73 \text{ \AA}$. This value is different from that for the Mg base alloys and closer to that in Al-Mn quasicrystals. While $a_R = 5.15 \text{ \AA}$ for $\text{Mg}_{32}(\text{AlZn})_{48}$ (Mukhopadhyay 1989), it is reported to be $4.60 \text{ \AA}$ for $\alpha(\text{Al-Mn-Si})$ (Henley and Elser 1986). The results obtained in the present case are also close to those reported for Ti_2Ni by Dunlap *et al* (1988) where $a_R = 4.76 \text{ \AA}$.

3.1c Distortions in the shape of diffraction spots: An enlarged 5-fold diffraction pattern of the quasicrystal is shown in figure 3. Subtle variations in peak intensity and shape of the spots exist compared to the ideal quasicrystalline diffraction pattern. It is observed that the inner ring of diffraction spots is weak and pentagonal, are more intense while the reverse is the case in Al-Mn quasicrystals. Further, it is noticed that the innermost diffraction spots close to the transmitted spot are not circular but triangular in shape. The vertices of the triangle are pointing towards the central spot. The shape of the diffraction spot changes from triangular to circular at higher $\vec{g}$ values. The second generation spots are neither perfectly triangular nor circular. The diffraction spots closer to the transmitted spot in the 2-fold pattern are also not perfectly circular. It is also noticed that the diffraction spots comprising the inner pentagons are triangular in shape. The circumferential deviation of the

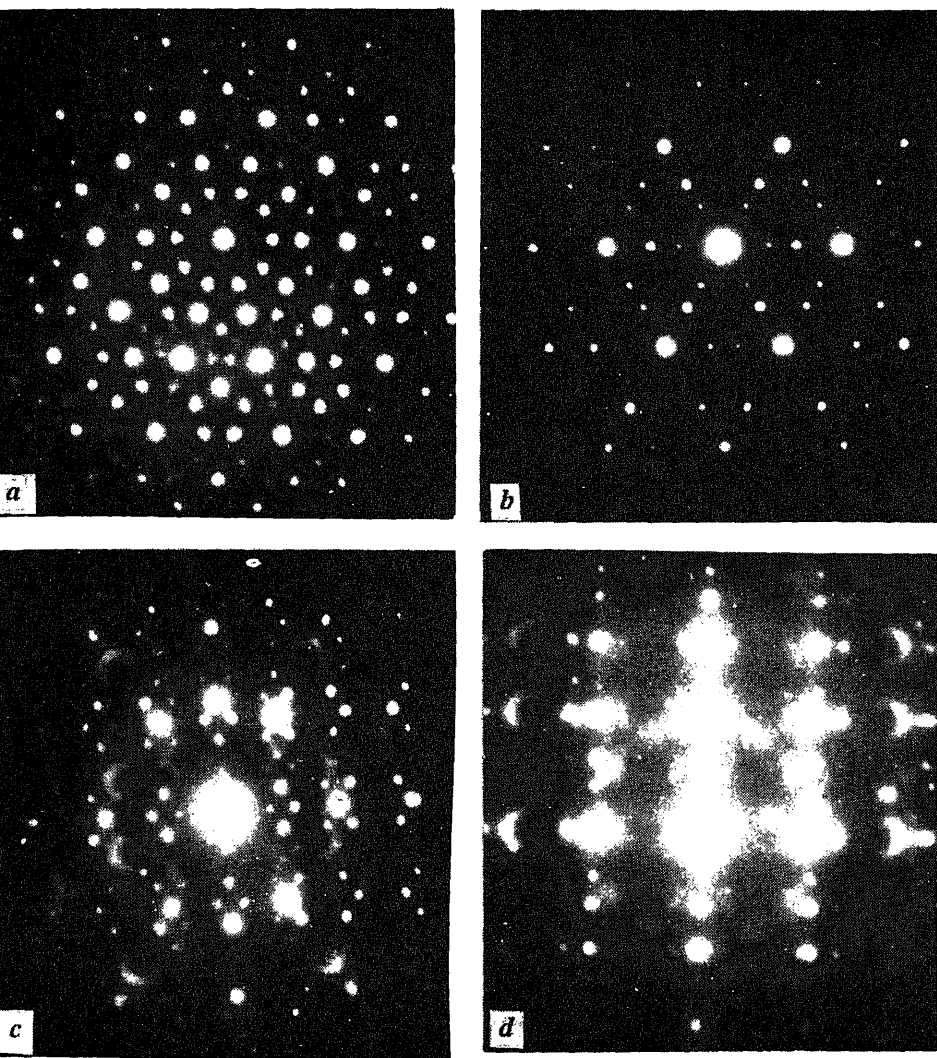


Figure 2. a. 5-Fold, b. 3-fold, c. 2-fold and d. $[\bar{1}10]$ SAED patterns from the I-phase.

diffraction spots can be noticed in the 5-fold pattern of the sample annealed at 73 K (figure 4).

Observations of the shape distortion of diffraction spots have been reported in $\text{Al}_{78}\text{Cr}_{17}\text{Ru}_5$ (Bancel and Heiney 1986), Al-Li-Cu (Yu *et al* 1987) and Mg-Al-Zn alloys (Chandra and Suryanarayana 1988). Various models and theories have been proposed to explain the observed shape distortion of the diffraction spots. Lubensky *et al* (1986) attributed these distortions to the presence of disorder in the quenched state of the quasicrystal. Socolar and Wright (1987) pointed out that the peak broadening in XRD and distortions of the spots in SAED patterns are the result of the anisotropic strain in the phason field of the icosahedral quasicrystalline phase. Zhang and Kuo (1987) explained these on the basis of local translational

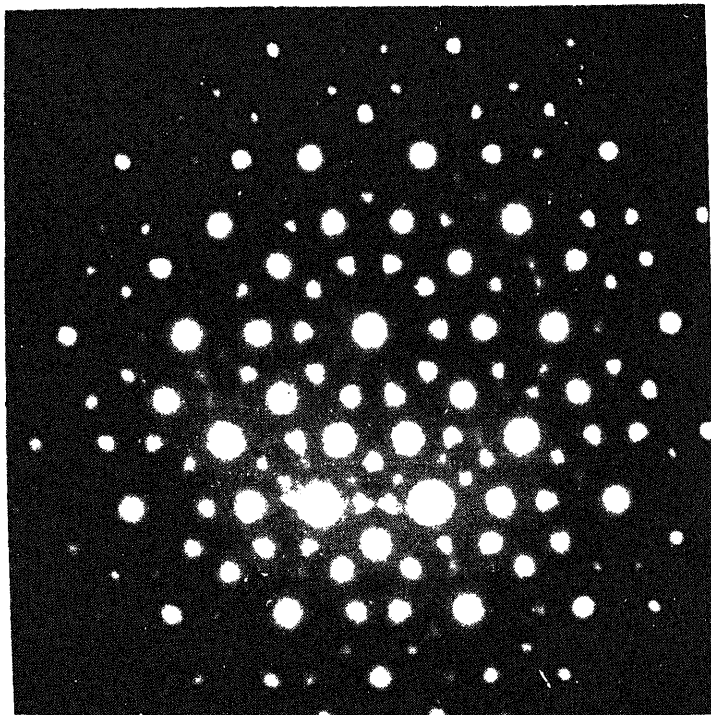


Figure 3. Enlarged 5-fold SAED pattern in Ti-37% Mn alloy showing triangularly distorted inner spots.

order occurring on several two-fold directions normal to the five-fold axis in different subgrains of the quasicrystal. An explanation based on rational approximant structure has been advanced for the observed distortions without taking support of the phason strain concept (Mukhopadhyay 1989). In our study due to the limited observations it has not been possible to propose any model. However, it is possible that any one or combinations of the models proposed earlier could explain the shape distortions of the diffraction spots.

3.1d Diffuse intensity: Arcs of diffuse intensity have been observed in the electron diffraction patterns of Ti-37% Mn in rapidly quenched and annealed conditions (Gibbons *et al* 1989; Bhaskaran *et al* 1993). In Ti-Mn alloy the diffuse intensity occurs in the quenched state itself (figures 2c and d). This is to be compared to the Al-Mn alloy where it has been reported to manifest only after annealing the quasicrystal (Chattopadhyay and Mukhopadhyay 1987; Mukhopadhyay *et al* 1987b). The intensity of the arcs is stronger in Ti-Mn alloy (Bhaskaran *et al* 1993; Gibbons *et al* 1987) compared to the hitherto reported observations in Ti-Fe (Dong *et al* 1987), Mg-Al-Zn (Mukhopadhyay *et al* 1987a), Al-Mn (Chattopadhyay and Mukhopadhyay 1987; Mukhopadhyay *et al* 1987b) and Al-Li-Cu alloys (Goldman *et al* 1988). Mandal *et al* (1991) observed that additions of silicon up to 6% to Ti_2Fe resulted in I-phase. They also observed arcs of diffuse intensities similar to Ti-Mn quasicrystal.

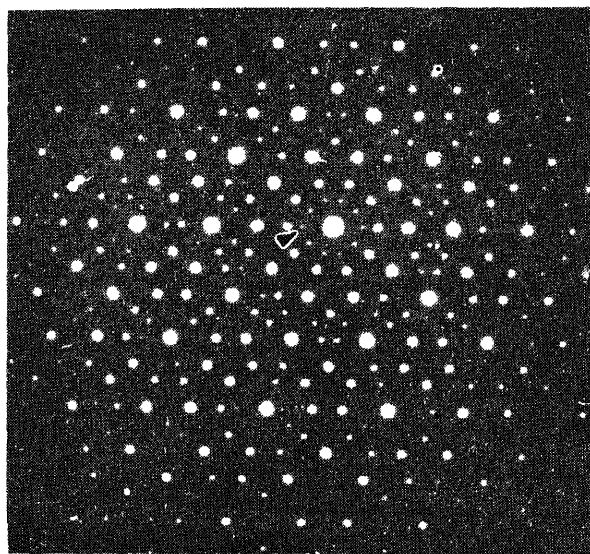


Figure 4. 5-Fold SAED pattern of Ti-37% Mn alloy after annealing at 573 K showing misalignment of spots.

In our earlier work (Bhaskaran *et al* 1993), annealing experiments were carried out to study the possible changes in the arcs of diffuse intensity. The diffuse intensities present in the 2-fold and $[\bar{1}10]$ patterns of the as quenched alloy were compared to those of the annealed sample. The results indicated that the arcs of diffuse intensities have given place to sharp diffraction spots upon annealing. It was noticed that the diffuse intensities together with the spots along the odd parity directions are quasiperiodic following τ inflation. The spots alone follow τ^3 scaling.

Figures 5a–f illustrate the results of tilting experiments carried out about a three-fold diffraction pattern. Even at a small tilt of 2° , one can notice the occurrence of triangular shape intensities and these are well developed at a tilt of 6° . Further tilting to 10.5° from, the three-fold orientation has resulted in $(\bar{1}10)$ pattern. At a tilt of 27° very strong arcs are noticed. The results of tilting from the 5-fold orientation about one of the 2-fold axis are shown in figures 6a–d. Arcs of diffuse intensities are noticed at a tilt of 4° and they are stronger at a tilt of 20° .

The existence of diffuse intensity in the electron diffraction pattern of Al-Mn quasicrystal was first reported by Mukhopadhyay *et al* (1987b) after annealing the quasicrystal. It was suggested that the diffuse intensities in Al-Mn quasicrystal are evidence for the short range order taking place before the onset of long range order. Henley (1988) showed that the locations of diffuse intensity at τ ratio on odd parity directions can be correlated to the existence of a face centered cubic quasicrystal. Experimental evidence for the existence of fcc type quasicrystal was obtained in Al-Cu-Fe system by Ebalard and Spaepen (1989). The 2-fold pattern of the I-phase in this alloy showed additional diffraction spots compared to the simple p type I-phase normally observed in Al-Mn alloys. These authors have proposed the existence of a fcc type I-phase to explain the presence of additional diffraction spots. Mukhopadhyay *et al* (1989) pointed out that the simple icosahedral

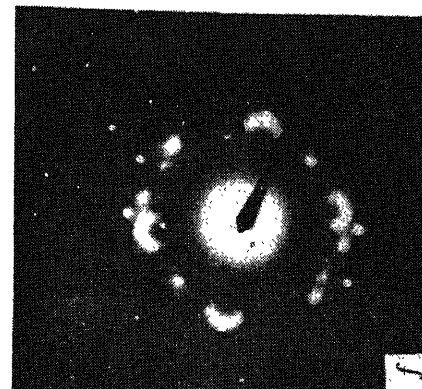
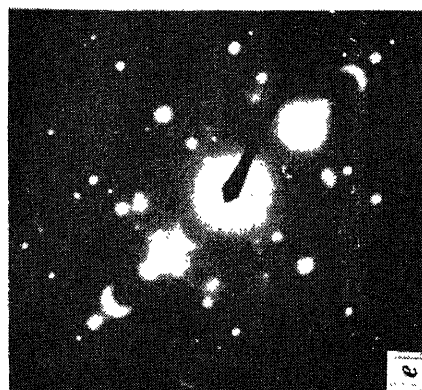
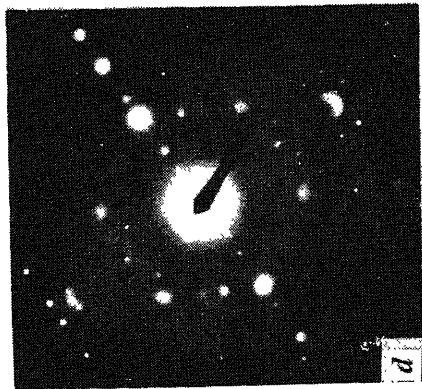
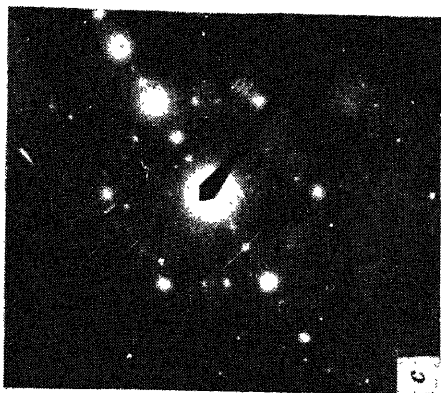
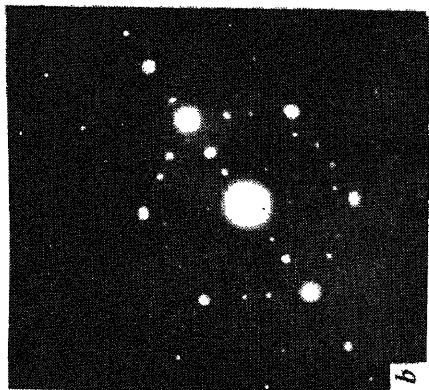
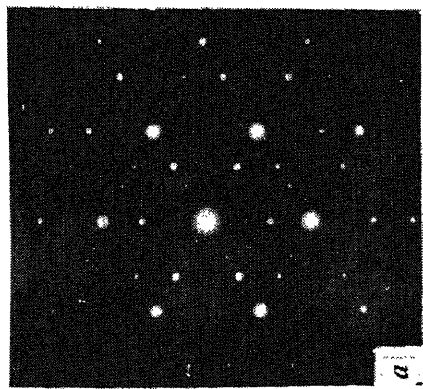


Figure 5. a. 3-Fold SAED pattern of the I-phase in Ti-37% Mn alloy. Patterns recorded after tilting about one of the 2-fold axis by b. 2°, c. 4°, d. 6°, e. 10.5° and f. 27°.

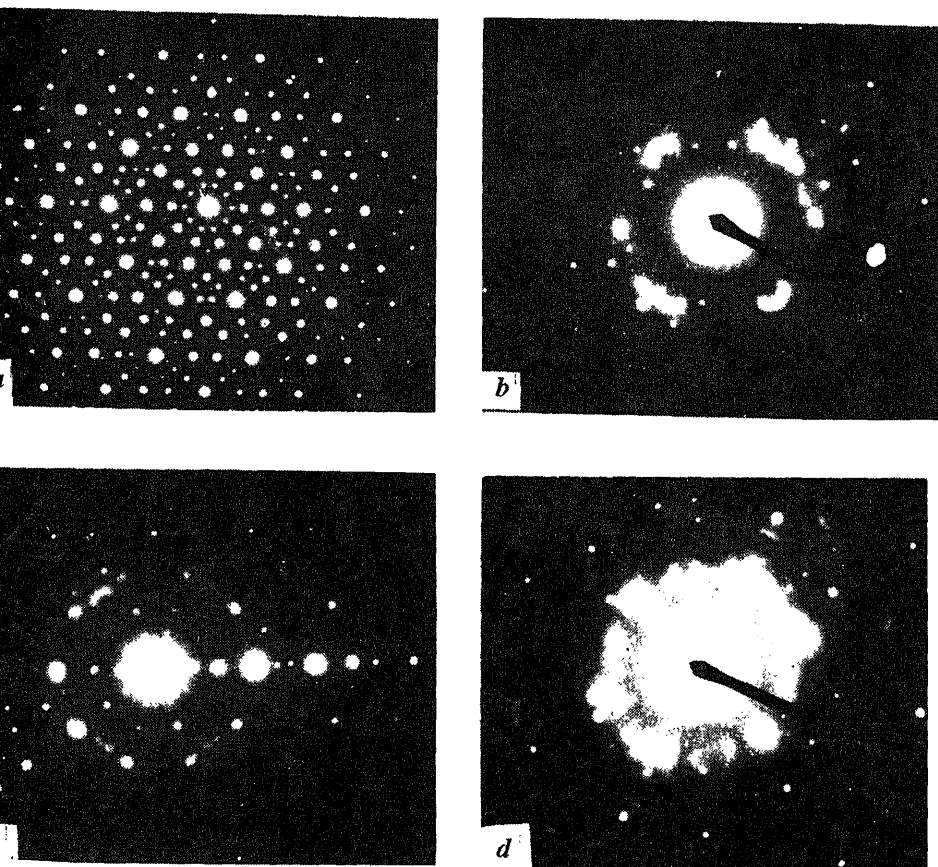


Figure 6. a. 5-Fold SAED pattern of the I-phase in Ti-37% Mn alloy. Patterns recorded after tilting about one of the 2-fold axis by b. 4°, c. 10° and d. 20°.

face centered icosahedral ordering transformation takes place in Al-10% Mn alloy when annealed at a higher temperature and the superlattice spots appear in place of diffuse intensity. Tsai *et al* (1990) reported that the I-phase formed in Al-Mn-Pd is a superstructure of the simple icosahedral quasicrystal similar to the 1D type icosahedral phase reported in Al-Cu-Fe system. From the above studies it is evident that the occurrence of diffuse intensity in the diffraction patterns have indicated the existence of I-phase other than the primitive type.

The results of Gibbons *et al* (1989) in Ti-Mn indicated that the experimentally observed arcs of diffuse intensity could be explained based on the icosahedral-glass model than on a model based on the transition state theory. The present observations of arcs of diffuse intensity are to be viewed in the context of the above mentioned studies.

1.1. Rational approximant structure: Figures 7a–b show the metastable crystalline phases present in the rapidly quenched alloy. In figure 7a it is noticed that some of the grains exhibit a faulted structure. Closer to this phase a strongly diffracting phase is also noticed in figure 7b. The selected area diffraction pattern from the

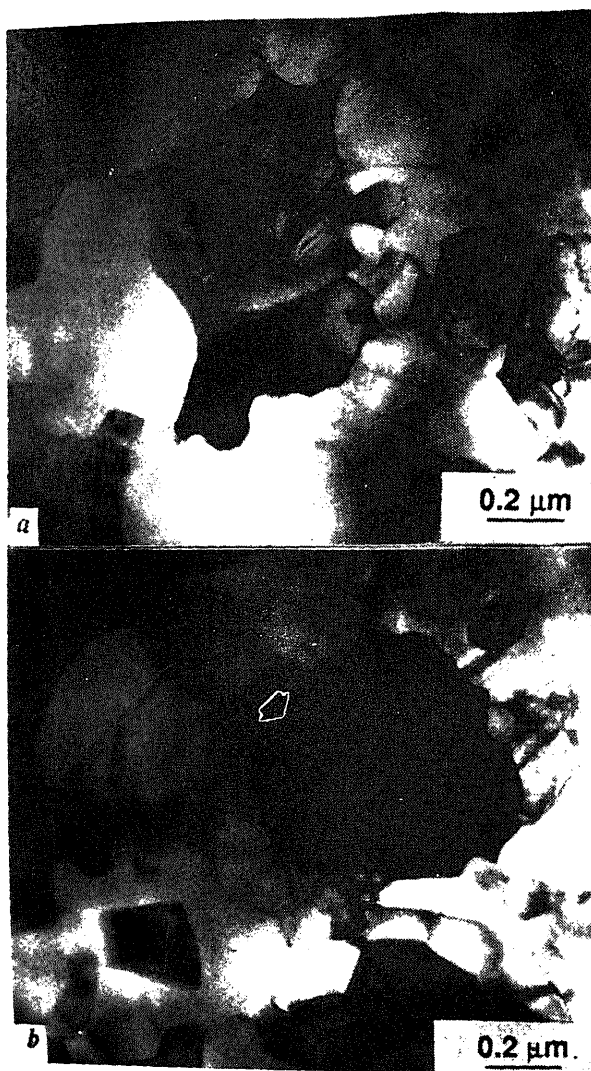


Figure 7. TEM of the metastable phases present in Ti-37% Mn alloy along with the τ -phase. In a, faults are seen and b, shows the phase (marked by arrow) giving a pseudo 5-fold diffraction pattern.

strongly diffracting phase is shown in figure 8. The diffraction pattern corresponds to the pseudo-five-fold symmetry. The inner spots marked by arrows in the diffraction pattern are approximately in the τ ratio. This pattern could be indexed in terms of a bcc structure with a lattice parameter of 21.7 Å.

Elser and Henley (1985) showed that the α -(AlMnSi) crystal structure is closely related to that of the icosahedral quasicrystal in Al-Mn-Si alloys. By modifying the projection construction of the three-dimensional Penrose tilings adopted to generate the quasiperiodic structure, they were able to generate periodic structures and correlate the cubic α -(AlMnSi) structure as an approximant structure of the

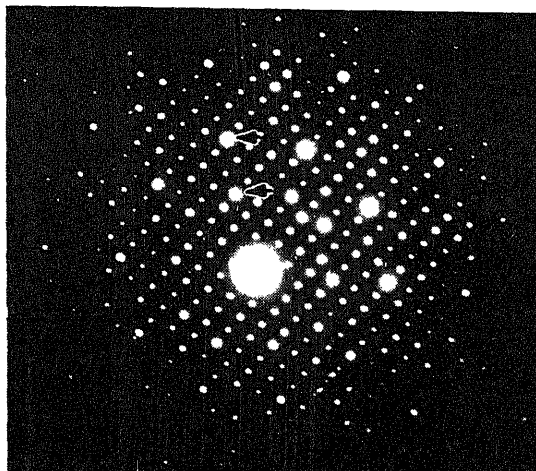


Figure 8. SAED pattern from the metastable phase shown in figure 7b exhibiting pseudo 5-fold symmetry.

icosahedral quasicrystal I-(AlMnSi). The lattice constant (a_c) of the approximant cubic structure is related to the quasicrystalline constant a_R .

For the 1/1 rational approximant structure, the cubic lattice constant is given by

$$a_c = [X] \cdot \tau,$$

where

$$X = [(2 + 2/\sqrt{5})^{1/2} \cdot a_R].$$

For the 2/1 approximant structure the lattice constant is given by

$$a_c = [X] \cdot \tau^2.$$

Substituting $a_R = 4.73 \text{ \AA}$ for the Ti-Mn quasicrystals, the 1/1 approximant structure has a cubic lattice constant $a_c = 13.02 \text{ \AA}$. Similarly for the 2/1 approximant structure $a_c = 21.07 \text{ \AA}$. This suggests that the bcc phase observed in figure 8 is a 2/1 rational approximant to the quasicrystalline phase.

Holzer *et al* (1989) have observed a bcc phase with $a = 13.44 \text{ \AA}$ after annealing the icosahedral quasicrystals in Ti-Mn alloy at 1275 K for 30 min. In this alloy, however, the cubic phase observed by them may correspond to a 1/1 approximant. Similarly, Dong *et al* (1987) have also reported a phase designated as α with $a = 13.6 \text{ \AA}$.

3.1f Decagonal like phase: In addition to the observations reported above, it was often noticed that very fine crystallites existed surrounding the icosahedral phase in the rapidly quenched alloy. These fine crystals showed striated contrast (figure 9). The SAED patterns from these phases seem to be very complex (figures 10 a-c). The intense spots in the diffraction pattern are found to be in the τ ratio. In these diffraction patterns, less intense spots from a crystalline phase are seen to be



Figure 9. TEM showing decagonal like phase with striated contrast.

superimposed. The spots in figure 10a could be indexed as the $(\bar{7}2\bar{5}3)$ zone of a hexagonal phase. The lattice parameters of this hcp phase are $a = 8.0 \text{ \AA}$ and $c = 15.7 \text{ \AA}$ in conformity with the results of Levine *et al* (1992). Further, it was often found that the patterns exhibited extensive streaking. On tilting, the streaking is found to consist of many weaker diffraction spots. The diffraction pattern shown in figure 10c corresponds to the 3-fold pattern. While the spots along one of the 2-fold axis is in the τ ratio, the spots in the other two-fold directions are nearly commensurate. Further, one can notice that there is a shift in the spot positions. No ten-fold symmetry was observed. These patterns suggest that a decagonal like phase exists in Ti-Mn alloys following appropriate processing.

3.2 Quasicrystal in Ti-24 at% Mn-13 at% Fe alloy

The XRD data of the rapidly quenched alloy is shown in table 2. The diffraction peaks correspond to the I-phase and β Ti(Mn). It is observed that the edge vector is stronger than the vertex vector in Ti-Mn-Fe quasicrystal. The I-phase in this alloy (figure 11) also exhibits speckle contrast similar to that in the Ti-37 at% Mn alloy. The grain boundaries of the I-phase are found to be decorated by very fine particles. The size of the quasicrystal seems to be bigger than that in the binary alloy suggesting that iron helps stabilize the I-phase.

The SAED patterns corresponding the 5-fold, 3-fold and 2-fold orientations are shown in figures 12 a-c. In the 5-fold pattern it is seen that the inner spots are now more or less circular. However, the arcs of diffuse intensity in the 2-fold pattern are more intense in this alloy even in the quenched condition. They lie on the odd parity directions in the 2-fold patterns. Additional diffraction patterns about the $[\bar{1}10]$ axis and an intermediate zone axis shown in figures 12d and e exhibit strong arcs of diffuse intensity.

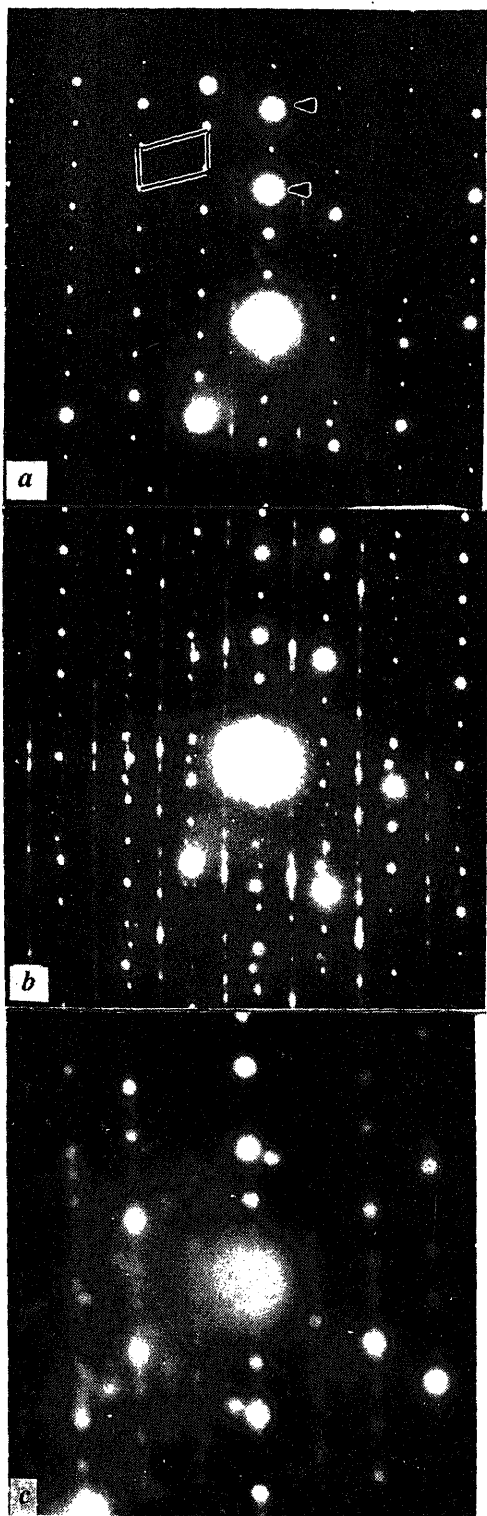


Figure 10. a-c. SAED patterns from the decagonal like phase showing quasiperiodicity along one direction.

Table 2. X-ray diffraction results of Ti-24% Mn-13% Fe in as quenched condition.

2θ	d (Å)	Intensity	Phase	Index
25.35	3.512	w	I	(1110 $\bar{1}$ 0)
28.7	3.108	w	I	(2210 $\bar{2}$ 0)
40.3	2.237	m	I	(100000)
40.95	2.203	w	β Ti; TiMn	(110); (320)
42.45	2.129	s	I	(110000)
71.60	1.317	w	I	(2110 $\bar{1}$ 1)

w, weak; m, medium; s, strong.

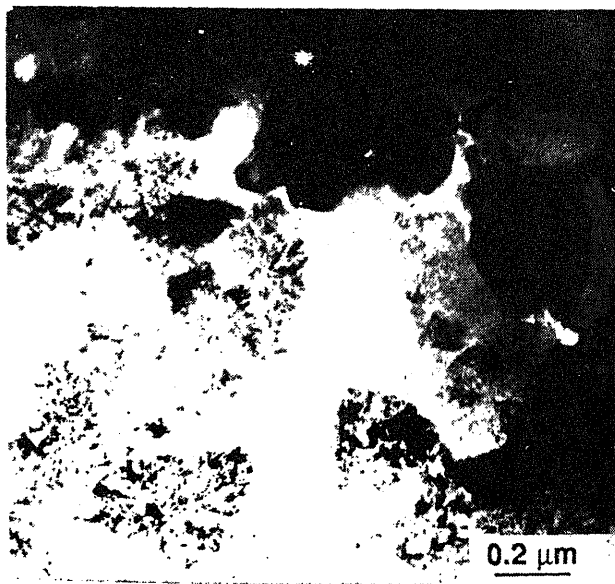


Figure 11. TEM of the I-phase in Ti-24% Mn-13% Fe alloy showing speckle contrast.

Following the method described in § 3.1b, the quasilattice constant for this alloy is calculated as $a = 4.74$ Å. This is not very different from the quasilattice constant for the I-phase in Ti-37 at% Mn alloy.

4. Conclusions

The formation of the I-phase in Ti-37% Mn and Ti-24% Mn-13% Fe have been followed by TEM studies. The shape distortions of the diffraction spots observed in this study are similar to those reported in the I-phase of other alloys. Arcs of diffuse intensity observed in the quenched alloy have given rise to a number of sharp but faint diffraction spots after annealing. These are compared with the arcs of diffuse intensity reported in Al-Mn, Al-Cu-Fe and other alloys. In addition to

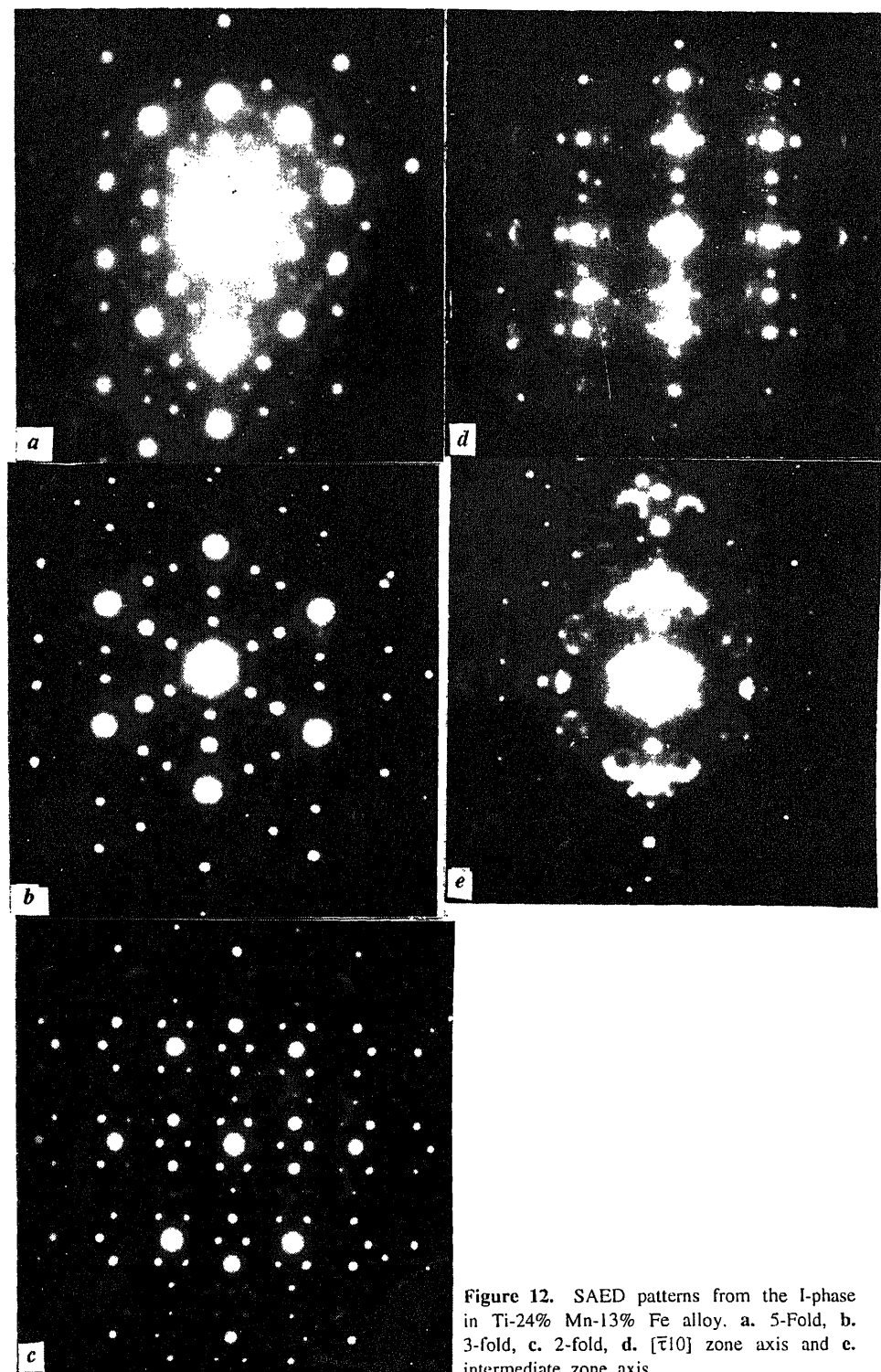


Figure 12. SAED patterns from the I-phase in Ti-24% Mn-13% Fe alloy. a. 5-Fold, b. 3-fold, c. 2-fold, d. $[110]$ zone axis and e. intermediate zone axis.

the I-phase, a rational approximant structure and another striated phase have also been observed in the Ti-37% Mn in the quenched state.

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Preparation and characterization of diamond films

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Abstract. Diamond films were deposited by magnetron sputtering of vitreous carbon disc and also by plasma CVD technique using $C_2H_2 + H_2$ or $CO_2 + H_2$ gas mixtures. The films were characterized by measuring the electrical, optical and microstructural properties. FTIR and Raman studies were carried out to study the effect of sp^2 and sp^3 bonds present in the films. The films had a high mechanical stress which was determined from the broadening of the optical absorption tail in the films.

Keywords. Diamond; chemical vapour deposition; sputtering; optical property; electrical property; microstructural study.

1. Introduction

Recently, diamond and diamond like carbon (DLC) films attracted much attention due to their high potential for various technological applications. During the last decade various laboratories throughout the world investigated the properties of diamond and DLC films and a large number of papers related to DLC, diamond or similar hard coating materials were published. In recent years, research efforts are mainly directed towards the preparation of diamond and DLC films for various device applications. Fabrication of high temperature, high power and high frequency semiconducting devices using diamond coating are of current interest to the researchers working in this field. Theoretical studies suggest that diamond devices may surpass Si or GaAs based devices provided several intricate problems which limit the prospect of diamond in device applications may be solved adequately (Collins 1992). Excellent reviews on the electronic properties of diamond and DLC films have been published (Collins 1989, 1990a).

There are various techniques reported so far, for the deposition of diamond films among which magnetron sputtering, variety of chemical vapour deposition (CVD), microwave plasma technique, plasma torch and ion beam deposition are worth mentioning (Badzian *et al* 1989; Chattopadhyay *et al* 1993; Bögli *et al* 1994). All the techniques have their individual merits and demerits. It has been observed that a low growth rate ($0.1\text{--}1\ \mu\text{m h}^{-1}$) was necessary for the production of good quality diamond films (Badzian *et al* 1989; Collins 1992). The main problem associated with increasing growth rate of diamond is that increase in the deposition rate is always associated with increase in the non-diamond sp^2 phase. Optical (FTIR) measurement is generally used to determine the ratio of sp^3 and sp^2 bonding in diamond films (Dutta *et al* 1993). Although the absorption associated with the non-diamond carbon (sp^2 bonding) may be reduced to a great extent by using suitable deposition condition, it was always found to be large in films compared to that in natural diamond (Collins 1990a). It has been observed that the growth

rate of CVD diamond films is increased with increase in the vol% of hydrocarbon in the gas mixture. But, it was also noticed that if the concentration of hydrocarbon is increased too much the non-diamond carbon in the film increases dramatically. Also, appreciable concentration of hydrogen is always found to be present in the deposited film and this excess H_2 generally makes the film highly stressed. Although successful growth of diamond requires the presence of atomic hydrogen, small amount of oxygen was observed to enhance the growth of diamond (Saito *et al* 1990; Chen *et al* 1992; Glumac and Goodwin 1992). Possibility of growing diamond films at lower deposition temperature (< 700 K) was also explored by several workers (Liou *et al* 1989; Ong and Chang 1989; Ihara *et al* 1991).

Choice of substrate is very important for growing diamond films for device application. Electronic grade diamond film requires the use of diamond substrate and diamond film is generally polycrystalline unless a diamond substrate is used. Single crystal diamond may be grown on cubic boron nitride (Koizumi *et al* 1990). But, single crystal BN is much expensive than using substrates of natural or high pressure synthetic diamond. Possibility of using other substrate materials was also explored. Growth of diamond on cheaper substrates coated with AIN may be useful due to lattice matching of the materials (Vasudev *et al* 1993). Polycrystalline diamond films, thus produced on non-diamond substrates, have important applications in microelectronic circuits, machine tool industry, optical coatings, X-ray windows, radiation detector and various other technological applications (Vermeulen and Harris 1977; Holiday *et al* 1992; Wu *et al* 1992; Ford 1994; Matthews and Eskildsem 1994). The high refractive index and surface roughness often limits the optical application of diamond film. DeNatale *et al* (1992) produced an antireflection coating on Ge substrate using polycrystalline diamond film to overcome the outstanding difficulties. Now, thermodynamic principles suggest that perfectly sp^3 bonded diamond may be produced at practically zero growth rate. This means whatever small growth rate is used for the production of polycrystalline diamond film, it will have considerable density of defect states, which will reside at the grain boundaries. Recently, much work is being done to understand the grain boundary scattering in polycrystalline diamond film (Liou *et al* 1989) with a view to make the films contain less defects so that the device quality may be improved to make it comparable or even better than that for Si and GaAs based devices.

The presence of grain (ordered) and grain boundaries (disordered) regions in polycrystalline film necessarily implies the existence of large amount of stress. Now, deposition of diamond films by plasma CVD technique would also culminate in additional inclusion of defects which may in turn add to the already existing mechanical stress due to the grain boundaries. A high compressive stress has been reported by many workers in diamond film (Wanlu *et al* 1992; Chattopadhyay *et al* 1994a). Wanlu *et al* (1992) indicated a decrease in compressive stress with increasing grain size. There are several research groups working on producing homo-epitaxial layers by CVD (Geis *et al* 1988; Fujimori *et al* 1990; Gildenblat *et al* 1990; Grot *et al* 1991) so that high temperature diodes and field effect transistors may be fabricated. The quality of the homoepitaxial layers produced at present are generally not adequate for the fabrication of devices and non-planar growth along with secondary nucleation are common (Badzian *et al* 1989) even on a diamond substrate. As a consequence, devices like microwave amplifiers (Brown 1987) or microcircuits with high packing density (Yoder 1987) has been

tried with an aim to produce devices workable at high temperature and high frequencies, higher than that achieved in GaAs or Si based devices (Simpson 1988). Diamond devices generally suffer from high series resistance (Gildenblat *et al* 1990; Grot *et al* 1991) when operated at room temperature. The optimum temperature of operation with low series resistance is ~ 770 K. But the conductivity of diamond at this temperature, even if doped, is not as good as Si at room temperature and is much lower than that for GaAs. Further, mobility of diamond film decreases with increasing temperature so that the frequency response becomes worse than that of GaAs devices at the same temperature.

Doping of diamond films have been considered by various workers (Gildenblat *et al* 1990; Glesener 1993; Tachibana 1993) for electronic applications. Diamond always has *p*-type conductivity and *n*-type diamond does not exist. Boron doping is very effective to make the film *p*-type. Doping of diamond to make it *n*-type is another intricate problem, which could not be solved although it is very important for the fabrication of devices. Doping with arsenic was tried by several workers to have *n*-type films but it was not successful. No technique has yet been developed to impart *n*-type conductivity to diamond film thus ruling out the possibility of bipolar devices. As such, high power devices with diamond may not be viable unless further developments are made. But devices with *p*-type doping were successfully produced by different workers. Glesener *et al* (1991, 1992) studied the Schottky diode of diamond and aluminium, for which they deposited boron doped diamond films by CVD of $\text{CO}_2 + \text{H}_2$. Boric acid in methanol was used as the source of boron through which CO_2 was passed before introducing it into the deposition chamber.

For the last several years we are working on the preparation and characterization of diamond and DLC films by different methods, e.g. magnetron sputtering of vitreous carbon and CVD techniques. For CVD techniques we have used different precursors like $\text{CO}_2 + \text{H}_2$ and $\text{C}_2\text{H}_2 + \text{H}_2$. In this communication, we report our studies on diamond films produced by different techniques and characterized by measuring the electrical, optical and microstructural properties.

2. Experimental

Diamond films were deposited on different substrates (e.g. Mo, glass, mica, Si and quartz) by d.c. magnetron sputtering or CVD with substrate temperature (T_s) within 500–1200 K. High substrate temperature always favoured the nucleation of diamond crystallites.

2.1 Magnetron sputtering technique

A vitreous carbon disc (of dia ~ 5 cm and thickness ~ 2 mm) was used as the target for producing diamond films by dc magnetron sputtering using a mixture of argon and hydrogen. The details of the apparatus and the technique have been reported elsewhere (Chattopadhyay *et al* 1993). The sputtering (at 1.5 kV and 20 mA) was carried out at different partial gas pressures ranging from 10^{-2} to 10^{-3} Pa with 5–10 vol% of hydrogen in $\text{H}_2 + \text{Ar}$ gas mixture.

2.2 CVD technique

We also deposited diamond films by CVD technique by using either $C_2H_2 + H_2$ or $CO_2 + H_2$ gas mixtures. The gas mixtures were cracked inside a conventional deposition chamber backed by rotary and diffusion pumps.

2.2a From $CO_2 + H_2$: Diamond films were produced by d.c. plasma deposition of CO_2 (3–5 vol%) and hydrogen mixtures (Chatterpadhyay *et al* 1994b). The films produced by this technique were doped with boron by passing a portion of CO_2 through boric acid, dissolved in ethanol. Requisite mass-flow meter and needle valve arrangements were incorporated so that the gas mixture, passing through the solution of boric acid in ethanol could be introduced into the deposition chamber at a controlled rate. A thermocouple was inserted by means of a vacuum feed-through into the chamber to measure the substrate temperature.

2.2b From $C_2H_2 + H_2$: For the deposition of diamond from $C_2H_2 + H_2$ gas mixture, a deposition chamber similar to that used for CVD of $CO_2 + H_2$ was used with only exception that we introduced $C_2H_2 + H_2$ in different proportions (C_2H_2 varying within 1–10 vol%) instead of carbon dioxide + hydrogen gas mixture. It was observed that the films deposited with C_2H_2 in the range 1–5 vol% produced diamond films with higher band gap (> 3.5 eV), while films deposited with C_2H_2 above 5 vol% were diamond like carbon (DLC) with lower band gap (1.5–2.8 eV) (Dutta *et al* 1993).

3. Results and discussion

3.1 Structural studies

The structure and surface morphologies of the diamond films were studied by XRD, TEM and SEM respectively. The XRD pattern of a representative diamond film prepared by magnetron sputtering of a vitreous carbon target is shown in figure 1. Strong reflections from (111), (220) and (311) planes could be observed for films deposited on molybdenum and mica substrates kept at ~ 900 – 1200 K during deposition. The above feature compared well with those observed by Celii *et al* (1992) and Guo and Yu (1992) for diamond films grown by CVD on silicon and molybdenum substrates. The lattice constant (a) evaluated from XRD studies was equal to 0.3583 nm which compared well with that obtained by Sawabe and Inuzuka (1986). The crystal size evaluated from the SEM micrographs was found to lie within the range of 0.3–0.6 μm (figure 2). An additional peak at 53.4° for Mo_2C could be observed in the XRD pattern for diamond films deposited onto molybdenum substrates (figure 1). Films deposited at lower substrate temperature than 850 K did not indicate any appreciable peak in the XRD pattern.

Figure 2 shows the SEM and TEM micrographs for some representative films deposited onto mica, glass, molybdenum and freshly cleaved NaCl substrates. The substrate temperature of the glass substrate could not be increased beyond 650 K and as such definite diamond crystals could not be observed (figure 2a) in these films. The graphite phase predominated for the films deposited onto glass substrates. Number density of the crystallites increased appreciably (figure 2b) for films

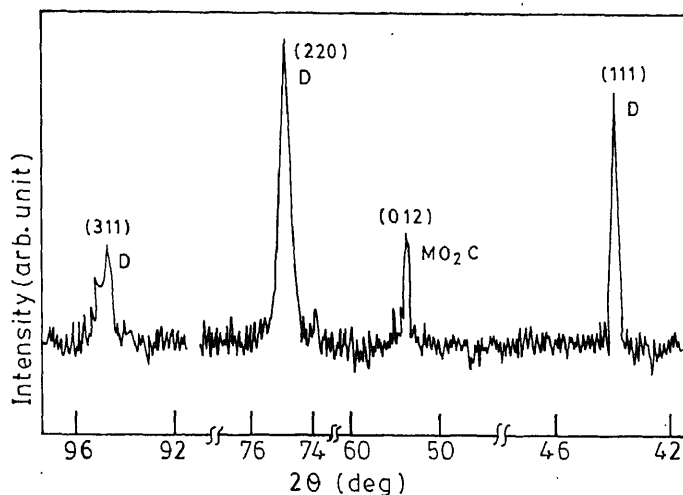


Figure 1. X-ray diffraction pattern of a representative diamond film deposited on Mo by d.c. magnetron sputtering of vitreous carbon target.

deposited onto mica substrates at the same temperature (~ 650 K). Films deposited onto molybdenum (figure 2c) and mica substrates (figure 2d) at temperatures between 1000–1200 K clearly revealed the cubic diamond crystals. The TEM micrographs for films deposited on to NaCl substrates at ~ 850 K indicated both polycrystalline (figure 2e, zone marked x) and single crystal zones (figure 2e, zone marked y) to be present in the films. The corresponding diffraction patterns indicated the presence of (111), (022), (113) and (004) planes. The SEM micrograph of the above film deposited onto NaCl crystal is shown in figure 2f.

The XRD traces of diamond films prepared by d.c. plasma deposition of CO_2 and hydrogen gas mixtures were similar to those observed in figure 1 for diamond films deposited from magnetron sputtering of vitreous carbon. Strong reflections were observed corresponding to (111), (220) and (311) planes at 44.1° , 75° and 94.5° respectively. The surface morphology of the diamond films was studied by SEM. Figure 3 shows the scanning electron micrograph of a representative diamond film on mica substrate. Cubic diamond crystallites are visible in the above micrograph in the background (zone A of figure 3a) of polycrystalline diamond, which has been shown separately in figure 3b.

Figure 4 shows the SEM micrographs of diamond films deposited on different substrates (mica, quartz and silicon) from cracking of acetylene and hydrogen gas mixture by a d.c. field. It can be seen that the nucleation density is higher for films deposited on silicon substrate. This may perhaps be due to the fact that silicon is a carbide forming material and as such may favour the nucleation of diamond film on it. The XRD pattern for these films was also characterized by the presence of strong peaks of (111), (220) and (311) planes.

3.2 Raman studies

The quality of the diamond films was studied by Raman spectroscopy. Raman shift

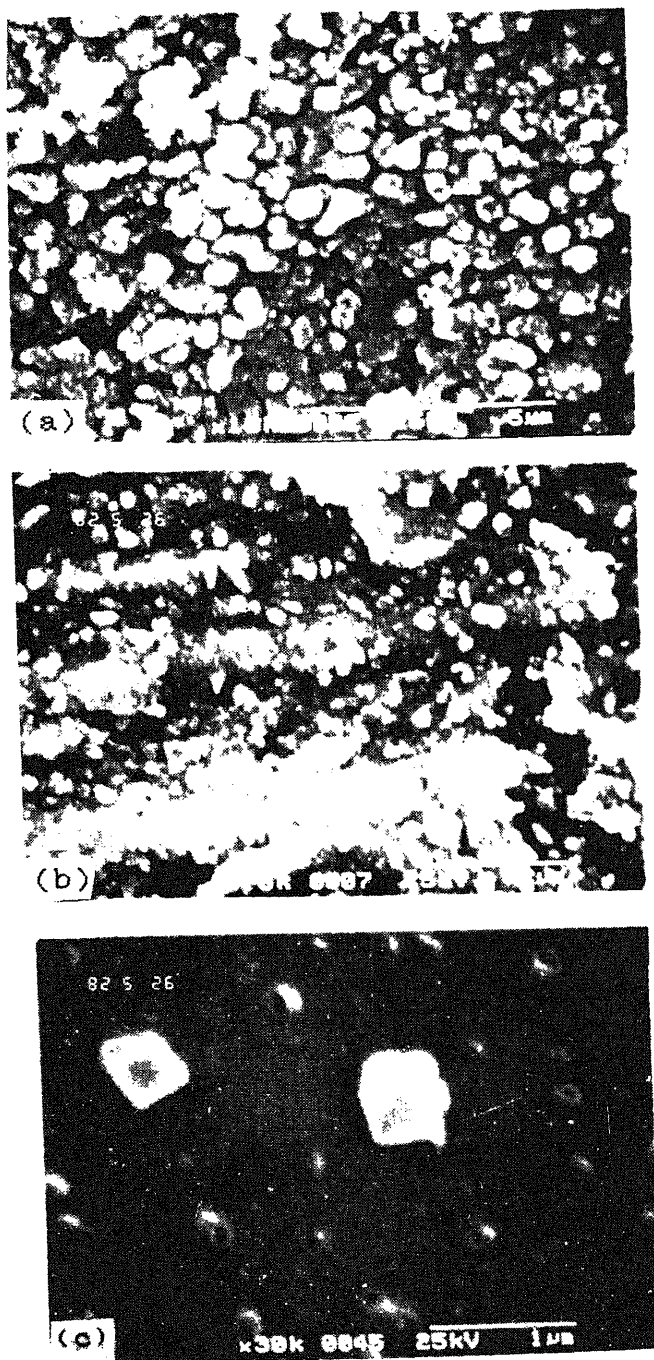


Figure 2a-c.

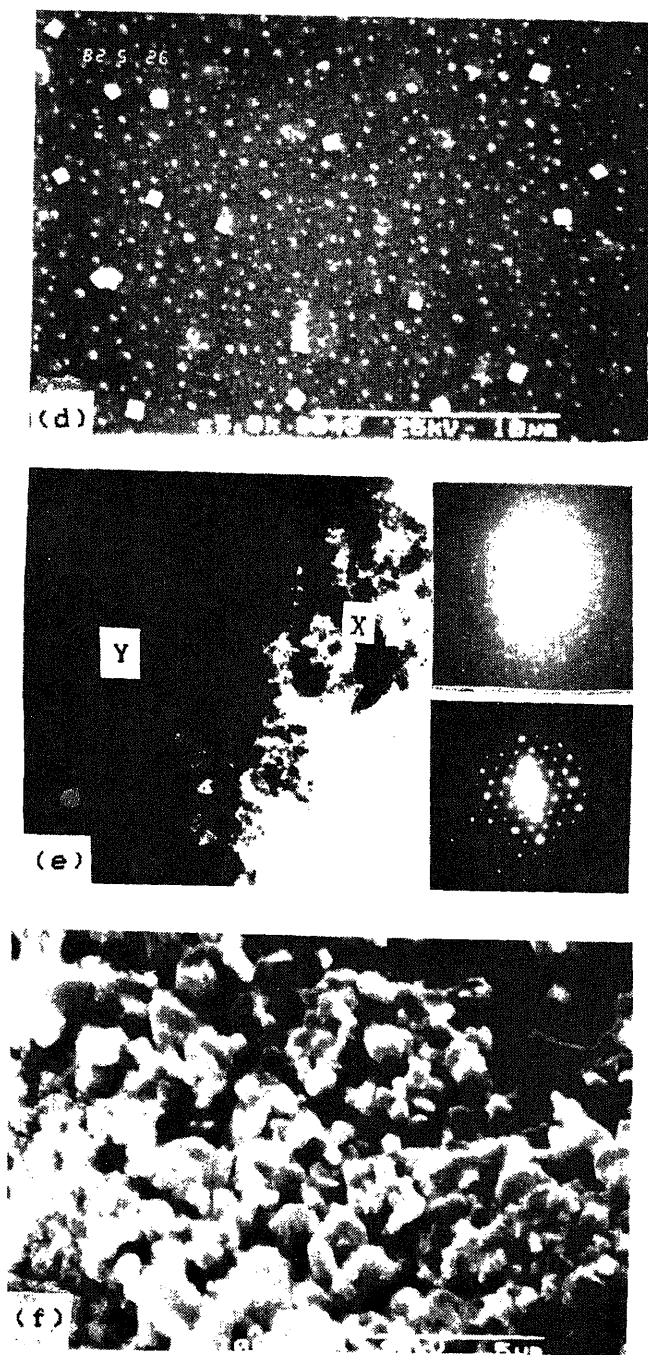


Figure 2. SEM (a, b, c, d and f) and TEM (e) micrographs for some representative diamond films deposited by d.c. magnetron sputtering of vitreous carbon target onto different substrates: a. glass (at $T_s \sim 650$ K), b. mica (at $T_s \sim 650$ K), c. molybdenum (at $T_s \sim 1200$ K), d. mica (at $T_s \sim 1200$ K), e. NaCl (at $T_s \sim 850$ K with polycrystalline zone, marked X, and single crystalline zone, marked Y), T_s being the deposition temperature.

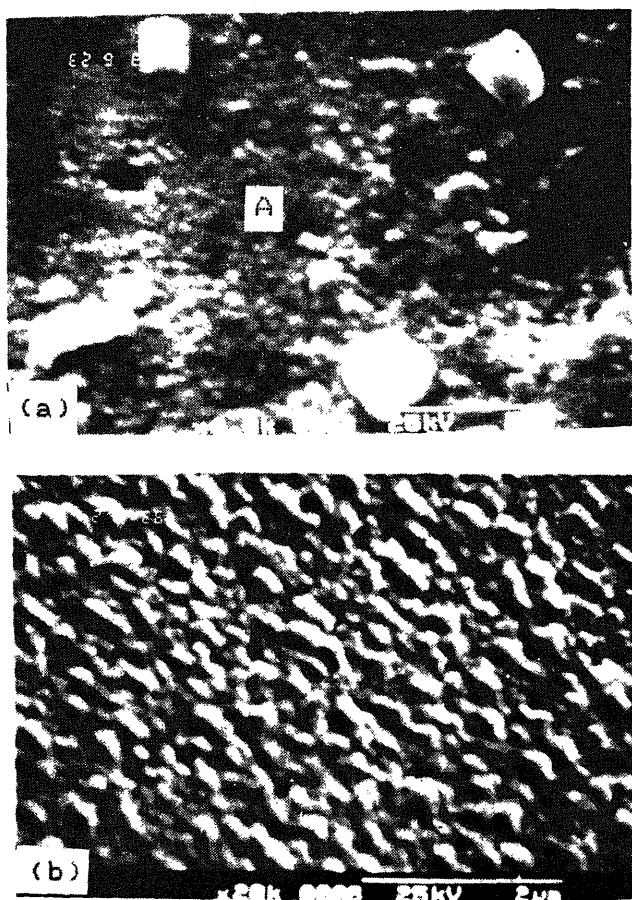


Figure 3. SEM of a representative diamond film deposited by CVD of $\text{CO}_2 + \text{H}_2$ (~5 vol% CO_2) on mica substrate. Cubic diamond crystallites are visible in the background (zone A of figure a) of polycrystalline diamond, shown in b.

was recorded in the wave number range $1200\text{--}1700\text{ cm}^{-1}$. Two Raman bands centred at 1332 cm^{-1} and 1550 cm^{-1} were observed for most of our films deposited on Si. Formation of diamond was confirmed by a sharp peak at the wave number 1332 cm^{-1} . Figure 5 shows the Raman shift of a film deposited with 4 vol% of C_2H_2 on Si at 900 K. sp^3 bonding in film corresponds to the small peak around 1331.8 cm^{-1} while the broad band near 1580 cm^{-1} was attributed to the non-diamond graphite component. The choice of the deposition parameters, mainly the hydrogen content and the substrate temperature during deposition, was varied to control the ratio of sp^3 to sp^2 bonding in the film.

3.3 Optical band gap

The optical band gap of diamond was measured for films deposited on quartz and mica substrates by recording the transmittance vs wavelength traces in the range

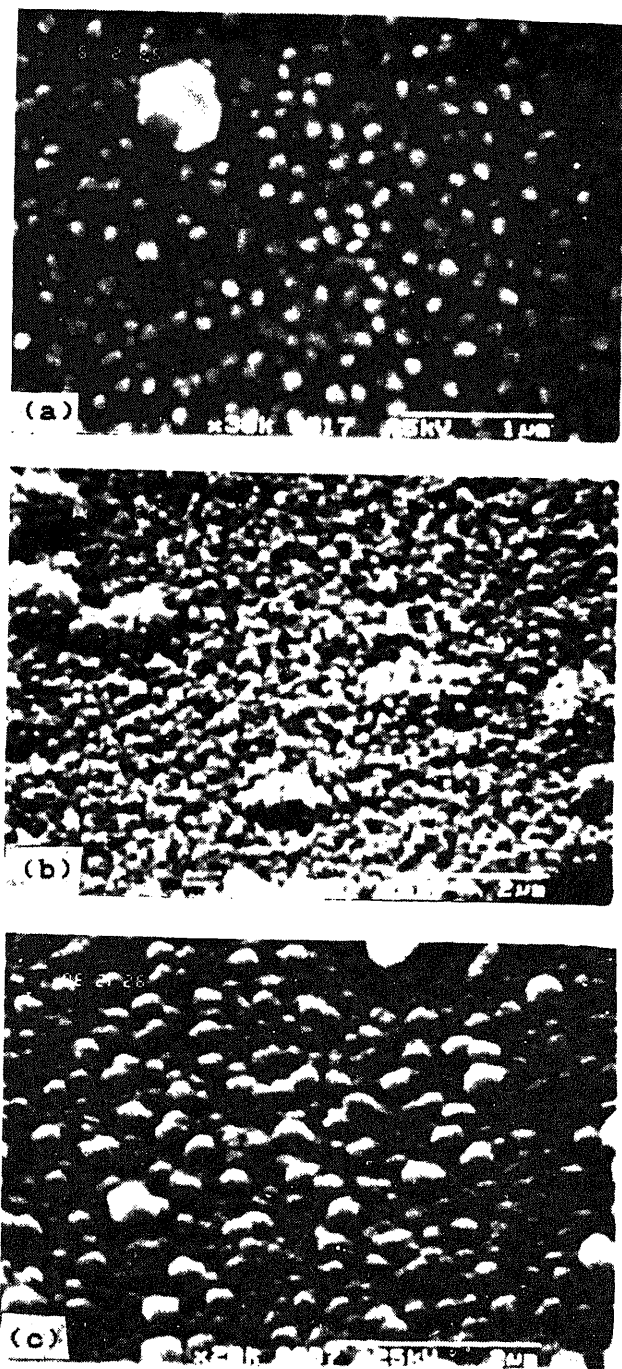


Figure 4. SEM of representative films deposited from CVD of $C_2H_2 + H_2$ (3–5 vol %) on different substrates: a. mica, b. quartz and c. Si.

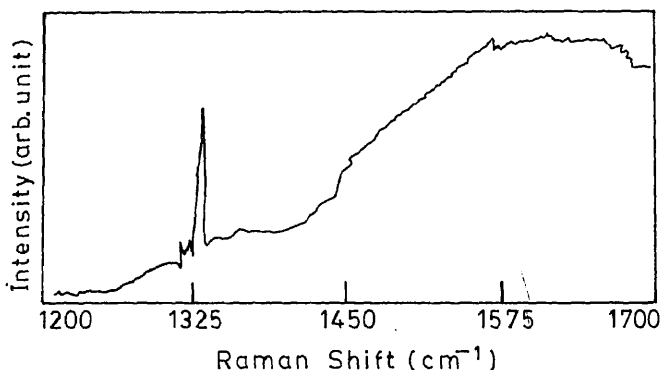


Figure 5. Raman shift of a representative diamond film deposited by CVD of $C_2H_2 + H_2$ (~4 vol% C_2H_2) on Si at ~900 K.

180–2000 nm by a spectrophotometer (Hitachi U-3410). The absorption coefficient (α) in the films varied with incident energy ($h\nu$) according to the relation:

$$\alpha h\nu = B (h\nu - E_g)^m, \quad (1)$$

where B is a proportionality factor, α the absorption coefficient and m , a parameter determining the nature of optical transition in the film.

For our CVD films deposited by cracking of acetylene and hydrogen gas mixture, we obtained both $m = 2$ and $m = 1/2$, as shown in figure 6. This indicates that both indirect and direct transitions may be present in the films which consisted of diamond crystallites embedded in amorphous non-diamond graphite phase. Films deposited with higher C_2H_2 (> 5 vol%) indicated predominant indirect transition with lower band gap (1.5–2.8 eV) while films deposited with lower C_2H_2 (~1–5 vol%) indicated predominant direct transition with higher band gap. The highest value of direct band gap obtained in our diamond film was ~4 eV. The refractive index of the films was found to vary within 1.8–2.4 with variation of λ within 860–1020 nm, as shown in the inset of figure 6. Films deposited from CVD of $CO_2 + H_2$ had direct band gaps within the range 3.8–4.0 eV with a very sharp absorption edge (Chattopadhyay *et al* 1994b).

Polycrystalline films are generally characterized by the presence of large number of grains joined together by the intercrystalline boundaries (grain boundaries) containing trap states. These trap states could effectively trap free carriers and in turn become charged giving rise to potential barriers at the grain boundary region. These grain boundary regions with inherent space charge layer result in band bending. The Franz-Keldysh effect arising out of the built-in electric field in a semiconducting material may be used to describe the excess absorption below the band gap energy and hence to determine the parameters describing the grain boundary phenomena in these films (Bhattacharyya *et al* 1993).

Diamond films are generally characterized by the presence of high stress (Nir 1987). Grain boundary defects in a polycrystalline film gives rise to the deformation potential and the consideration of the resulting field at the grain boundary region

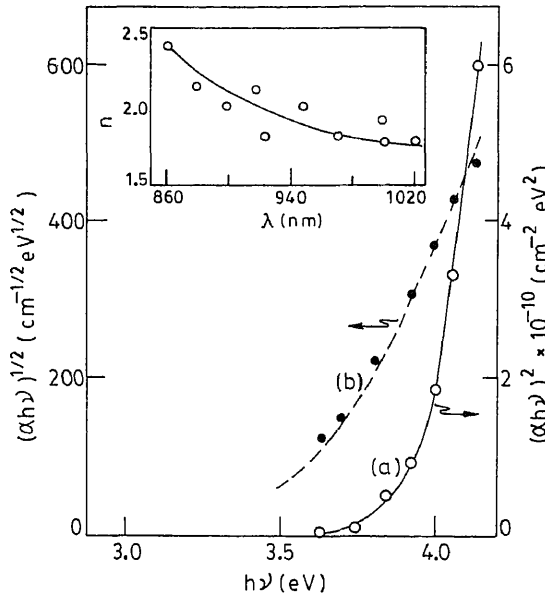


Figure 6. Plot of $(\alpha h\nu)^2$ vs $h\nu$ (curve a) and $(\alpha h\nu)^{1/2}$ vs $h\nu$ (curve b) for a representative diamond film deposited by plasma deposition of $C_2H_2 + H_2$ (~5 vol% C_2H_2) on quartz. Inset shows the variation of refractive index (n) with λ .

and the related induced interaction is very important in describing the grain boundary effects. Thus, besides the grain boundary electric field, the mechanical stress due to lattice distortion at the grain boundary regions which may include permanent lattice disorder and thermal lattice disorder, may also influence the electronic structure and hence the below band-edge optical absorption processes as a whole.

The influence of mechanical stress in the grain boundary region of polycrystalline films may be associated to the electrostatic fluctuations of the band gap (E_g) as has been indicated earlier by several workers (Szczyrbowski 1979, 1981; Klyava 1985; Gavrilenko 1987; Maity *et al* 1994a,b). The basic idea of the models considered by the earlier workers is the existence of a finite probability of indirect transitions between the states lying at different and same sites (Maity *et al* 1994a) in the polycrystalline sample. This will control the specific shape of the absorption tail in the below band gap region. Besides this indirect transition, allowed direct transition may also occur simultaneously in these polycrystalline films. But the latter will predominate only in the photon energy region $\hbar\omega \geq \bar{E}_g$. $\bar{E}_g$ is the average value of the fluctuating E_g in the grain and grain boundary regions. Thus, the contribution from the latter on the tailing of the optical absorption is not considered when effect due to grain boundaries are of primary importance.

Thus, one can get the total below band gap absorption coefficient $\alpha(=\alpha^E + \alpha^M)$ and hence the normalized absorption coefficient α/α_0 (α_0 being the absorption coefficient at the band gap) due to the combined effects arising out of the electric field (α^E) at the grain boundaries and the mechanical stress (α^M) present in polycrystalline films. The best fit of this simple theoretical model (Maity *et al*

1994b) to the experimental plots for films deposited from acetylene and hydrogen gas mixtures ($C_2H_2 < 5$ vol%) is shown in figure 7. This will provide unblemished values of the grain boundary potentials (E_b) and the density of trap states (Q_t) of polycrystalline semiconductor films. The fitting parameters used for this purpose were $\bar{n}=2.0$, $a=0.358$ nm and $m^*=0.80 m_o$, where $\bar{n}$, a and m^* are the average values of refractive index, lattice constant and effective mass of the carriers respectively. The values of the direct band gap (E_{gd}), average grain size ($\bar{L}$) and the absorption coefficient (α_o) at the band gap were also used for the above computer fitting (Chattopadhyay *et al* 1994a).

It may be noticed (figure 7) that the experimental data showed an excellent agreement with the theoretical variation throughout the whole range of measurements provided we consider the contribution of the mechanical stress in the diamond films. We have obtained the values of E_b and Q_t from the values of K (inverse of the Debye length) and F_s (electric field at the grain surface), obtained from the best fit of the data by using the following expressions (Bhattacharyya *et al* 1993),

$$Q_t = \epsilon F_s / q, \quad (2)$$

and

$$E_b = q F_s / K. \quad (3)$$

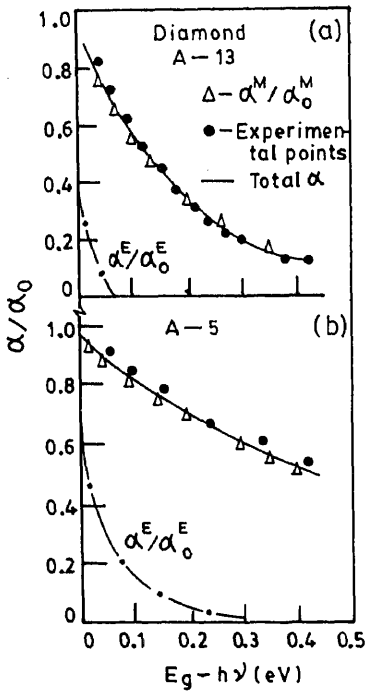


Figure 7. Variation of normalized absorption coefficient (α/α_0) with ($E_g - h\nu$) for diamond films deposited by CVD of $C_2H_2 + H_2$ (~1-5 vol % C_2H_2) on (a) quartz and (b) mica substrates. (—●—) experimental points along with theoretical plots; (---) with α^E only; ($\Delta\Delta\Delta$) with α^M only; (—) with both α^E and α^M .

It was observed that the barrier height (E_b) in our diamond films, deposited on quartz and mica substrates, varied within 0.36–0.40 eV, while the density of trap states (Q_t) varied within $0.4\text{--}2.6 \times 10^{13} \text{ cm}^{-2}$.

Now, the strains ($\Delta a/a$) in the films may be evaluated from the value of a disorder factor (σ') used (Maity *et al* 1994a, b) for the best fit of the above α/α_0 vs $E_g - h\nu$ plot (figure 7). The corresponding relations are given in Maity *et al* (1994a) while the relations related to σ' and $\Delta a/a$ are given in Maity *et al* (1994b). The stresses in the films were generated by using the bulk value of the elastic constant (Madelung 1987). A small decrease in stress was observed for films deposited at higher substrate temperatures (T_s) which attained a plateau region above $\sim 770 \text{ K}$. The trap states varied within $0.4\text{--}2.6 \times 10^{13} \text{ cm}^{-2}$ with the decrease in T_s from 770 to 570 K. This would mean that films having higher density of trap states (Q_t) would contain more stress. The values of the stress ($2.2\text{--}9.3 \times 10^9 \text{ dynes cm}^{-2}$) evaluated as above compared well with those obtained by Wanlu *et al* (1992), who reported a decrease in the compressive stress with increasing grain size in diamond films deposited from methane and hydrogen by d.c. plasma chemical vapour deposition technique. The analysis presented above showed that the mechanical stress contributes significantly in explaining the absorption band tail of polycrystalline diamond films.

3.4 FTIR studies

The formation of well defined diamond crystallites is dependent on the C/H ratio in the film along with the rate of deposition. Higher C/H ratio and growth rate result in diamond like films. FTIR studies were used to determine the C/H ratio in the films produced by cracking $\text{C}_2\text{H}_2 + \text{H}_2$ gas mixture. Figure 8 shows FTIR spectrum of a representative film deposited on Si by using a gas mixture containing 4 vol% C_2H_2 and 96 vol% H_2 within the wavenumber range $400\text{--}4000 \text{ cm}^{-1}$. The spectrum shows different vibrational modes. The large intensity of the peak at 1450 cm^{-1} compared to that at 1375 cm^{-1} would be indicative of a shift from sp^2 to sp^3 bonds.

The tail of the absorption edge in the NIR region can be described by (Dutta *et al* 1993):

$$\alpha = \alpha_{\infty} \exp (\nu/\nu_0) \quad (4)$$

where ν_0 is the resonant frequency of the corresponding oscillator. The values of α_{∞} and ν_0 were determined from the intercept and the slope of the plot of $\ln(\alpha)$ vs wavenumber (ν). The variation of α with ν for diamond films was determined for several representative films and was found to be of the form:

$$\alpha = 1569 \exp (\nu/7095) \text{ for films with 5 vol\% } \text{C}_2\text{H}_2,$$

and

$$\alpha = 463 \exp (\nu/8536) \text{ for films with 8 vol\% } \text{C}_2\text{H}_2.$$

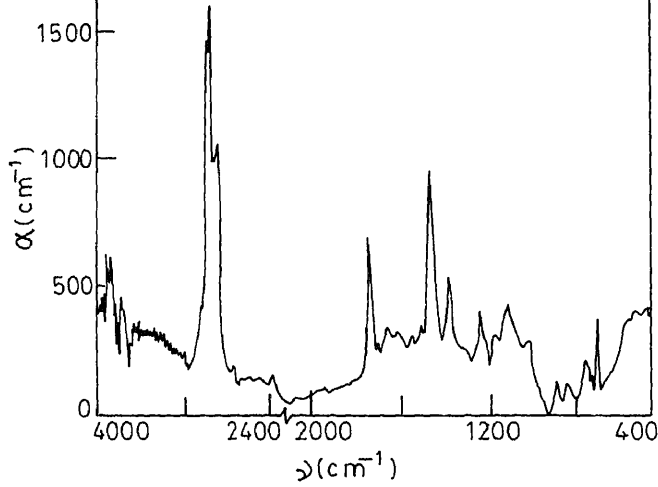


Figure 8. FTIR of a representative diamond film deposited with $C_2H_2 + H_2$ (~4 vol% C_2H_2).

The approximate H/C ratio in diamond film is very important since it determines the ratio of sp^3/sp^2 bonding and the shape and size of diamond crystallites. The H/C ratio in our diamond film was estimated from the absorption strength of the C-H stretching mode at 2800–3100 cm^{-1} (Dutta *et al* 1993). The hydrogen content (C_H) is related to the absorbance $\alpha(q)$ by:

$$C_H = 2.303 (K_0 d)^{-1} \int_{q_1}^{q_2} \alpha(q) q^{-1} dq, \quad (5)$$

where d is the sample thickness in cm and q_1 and q_2 are the wave numbers at both the edges of the absorption peak and K_0 is a constant in cm^2/mol which is determined from a standard material containing C-H bonds. We have taken $K_0 = 7.8 \times 10^2$ so that C_H in our films varied within 0.08–0.09, which compared well with that reported by others (Yasuda and Komiyama 1990; Phillips *et al* 1992).

3.5 Electrical conductivity

The electrical conductivity (σ) and Hall mobility (μ) of the diamond films produced by CVD of $CO_2 + H_2$ with different amount of boron doping were measured over a wide range of temperature. The activation energies (E_a) in the films decreased with increasing boron concentration. The films showed a predominant p -type conductivity as determined from Hall effect measurements. The variation of σ and μ with temperature exhibited two distinct slopes obeying the relations:

$$\sigma = \sigma_0 \exp(-E_a/kT), \quad (6)$$

$$\mu = \mu_0 \exp(-E_\mu/kT). \quad (7)$$

The carrier concentration (p) also indicated similar variation so that

$$p = p_0 \exp(-E_p/kT), \quad (8)$$

The measurement within the temperature range 90–500 K indicated

$$E_g = E_\mu + E_p, \quad (9)$$

as suggested by Petritz (1956). This shows that grain boundary scattering will effectively control the carrier transport phenomenon in these films. The presence of interface states along with thermionic emission across the grain boundaries will directly affect the charge transport mechanism in polycrystalline films and the Petritz model modified by Seto (1975) and Baccarani *et al* (1978) was considered so that the temperature dependence of mobility (μ) will determine the barrier height (E_b) following the relation:

$$\mu = L e [1/2 \pi m^* kT]^{1/2} \exp(-E_b/kT), \quad (10)$$

where L is the grain radius in the film and m^* the effective mass of the carriers. Plot of $\ln(\mu T^{1/2})$ vs $(1/T)$ was a straight line and the slope of it gives E_b . The density of trapping states (Q_i) at the grain boundaries of the polycrystalline diamond films is given by (Seto 1975):

$$E_b = e^2 Q_i^2 / 8 \epsilon p, \quad (11)$$

where ϵ is the dielectric constant. E_b was found to decrease with increase in carrier concentration (p) indicating partial depletion of the grains in these polycrystalline boron doped diamond films in which $Lp \gg Q_i$ (Mitra *et al* 1994). It was observed that with the increase in doping density the carrier concentration (p) varied within 1.0×10^{17} to $5.0 \times 10^{18} \text{ cm}^{-3}$ and the corresponding variation of Q_i was within 6.0×10^{11} to $4.0 \times 10^{12} \text{ cm}^{-2}$.

4. Conclusion

Diamond films, deposited on different substrates (e.g. Mo, glass, mica, Si and quartz) by d.c. magnetron sputtering and CVD of $\text{C}_2\text{H}_2 + \text{H}_2$ or $\text{CO}_2 + \text{H}_2$ with substrate temperature within the range 500–1200 K indicated that a high substrate temperature (~1000–1200 K) always favoured the nucleation of diamond crystallites. The optical band gap of diamond films were determined and showed a wide variation within 1.8–4.0 eV depending on the deposition technique and the deposition condition. It was observed that the films deposited from CVD of $\text{C}_2\text{H}_2 + \text{H}_2$ (with C_2H_2 in the range 1–5 vol%) produced diamond films with higher band gap (>3.5 eV), while films deposited with C_2H_2 above 5 vol% were diamond like carbon (DLC) films with lower band gap (1.5–2.8 eV). A sharp band gap at ~4.0 eV was observed for films deposited by CVD of $\text{CO}_2 + \text{H}_2$ (3–5 vol% of CO_2).

TEM observations indicated the films to be polycrystalline. The effect of grain boundaries in the polycrystalline diamond films were studied from the below band

gap absorption measurements. A theoretical fit of the experimental data indicated grain boundary barrier height of $\sim 0.36\text{--}0.40\text{ eV}$ and the density of the trap states at the intercrystalline boundary region varied within $0.40\text{--}2.5 \times 10^{13}\text{ cm}^{-2}$. The effect of mechanical stress in the film (deposited by CVD of $\text{C}_2\text{H}_2 + \text{H}_2$) was also determined from the above optical measurements which indicated that the stresses in the diamond films varied within $2.2\text{--}9.3 \times 10^9\text{ dyne cm}^{-2}$. The quality of the films was studied by Raman effect which indicated a sharp peak at $\sim 1332\text{ cm}^{-1}$. These studies were correlated with FTIR observations.

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Deposition of diamond like carbon (DLC) and C–N films using ion beam assisted deposition (IBAD) technique and evaluation of their properties

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Abstract. Diamond like carbon films and C–N films were prepared using ion beam assisted deposition technique (IBAD). Tribological properties were studied by subjecting DLC coated films to the accelerated wear tests. These tests indicated a significant improvement in the mechanical surface properties of glass by DLC coating. Better wear features were obtained for thinner DLC coating as compared to the thicker ones. We also studied the optical properties and obtained a band gap of 1.4 eV for these films. An attempt was made to prepare C₃N₄ films by using IBAD. We observed variation in the nitrogen incorporation in the film with the substrate temperature.

Keywords. Ion beam assisted deposition; DLC films; C–N films; tribological properties; RBS analysis.

1. Introduction

Diamond like carbon (DLC) films and C–N films are subject of considerable interest due to their very special mechanical and optical properties. The DLC films are known to exhibit high value of hardness (Pethica *et al* 1985; Jiang *et al* 1990), chemical inertness (Dischler *et al* 1983; Mori and Namba 1984), and low sliding coefficient of friction (Enke *et al* 1980; Memming *et al* 1986). The C–N films are also expected to show similar or even superior properties as compared to the DLC films depending on the nature of the C–N bonding and the possibility of realizing a fraction of the dispersed (β -C₃N₄) phase, which is predicted to have a hardness greater than that of diamond (Liu and Cohen 1989, 1990).

The DLC films have been deposited by several methods such as dual ion-beam sputtering (Banks and Rutledge 1982; Nabot and Paidassi 1990; Deutchman *et al* 1991), hydrocarbon decomposition with pulsed, rf and dc plasma (Whitemell and Williamson 1976; Sokolowski *et al* 1979; Enke 1981), low energy ion bombardment (Khan and Woollam 1984) and Ar ion bombardment of evaporated carbon films (Spencer *et al* 1976; Fujimoro and Nagai 1984). The C–N films have been prepared mostly by dc magnetron sputtering (Chen *et al* 1993), rf sputtering (Kin Man *et al* 1994), shock compression of nitrogen containing organic materials (Wixom 1990), and pyrolysis of organic compounds having high nitrogen content (Leon Maya *et al* 1991) etc.

In the present paper we report ion beam assisted deposition (IBAD) of DLC

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films on glass/quartz and C-N films on single crystal silicon (100). IBAD involves the bombardment of thermally evaporated thin films by low energy ions (N_2^+ , Ar^+ etc.) during film growth. In our case we evaporate pyrolytic graphite with the simultaneous bombardment of Ar^+ and N_2^+ in order to have films of DLC and C-N, respectively.

Usually, crystal growth is promoted by elevating substrate temperature which enhances mobility of the deposited surface atoms. Higher temperature also leads to improvement in film-substrate adhesion by promoting a minimal required interface reaction. In the case of ion assisted deposition the energy deposited by the impinging ions provides the extra mobility without the need to raise the global temperature. The ion energy also produces atomic motion in the bulk by the so called atomic mixing phenomenon over a length scale of a few nanometres (Muller 1986a,b). This leads to higher film density and enhanced adhesion with the substrate.

2. Experimental

In our experiments, the DLC films were deposited on float glass, mineral glass and quartz whereas the C-N films were deposited on (100) oriented silicon. The deposition involved electron beam evaporation of pyrolytic graphite (Union Carbide Ltd.) using a 2 kW e-beam evaporator (Varian, model VT 922-0020) onto the substrates with simultaneous impingement of the growth front by energetic ions. The ions were derived from an 8 cm Kaufmann source (model ID 3501). The ion energy was varied from 100 eV to 1000 eV in different depositions. Use of an energy of 300–400 eV led to optimum film quality in the case of both the DLC and C-N films. The optimum ion flux for DLC deposition was about 0.35 mA/cm^2 (Ar^+) and that for the C-N films was 0.5 mA/cm^2 (N_2^+). The thickness was monitored with quartz crystal and the ion flux was measured with a Faraday cup. The thicknesses of DLC films were between 30 Å and 300 Å whereas those of C-N films were around 1000 Å. The substrates were held at ambient temperature during the deposition of DLC films whereas the C-N films were deposited at different substrate temperatures from 100–500°C. Deposition rates for DLC and C-N films were typically between 0.5 and 1 Å/sec, respectively. Optical properties of DLC films were studied using UV-VIS spectroscopy. Ball-on-disc type wear tester was used to assess the wear performance of DLC coated float glass samples *vis-a-vis* uncoated float glass sample. The C-N films were characterized using Raman and Rutherford backscattering spectroscopies.

3. Results and discussion

3.1 DLC films

To assess the wear performance of DLC coated samples, we assembled a ball-on-disc type wear tester in our laboratory. In this system a hard steel ball (diameter, 10 mm) was slid onto the sample for different periods of time at a speed of 300 revolutions per minute with a load of 50 g. Loss of the material due to the ball sliding over the sample was measured with the help of a microbalance with an

accuracy of 1 μg . Weight loss of the material as a function of time for constant rotational speed and load was studied. These values are given in table 1.

Figure 1 shows the weight loss of materials as a function of time for the uncoated glass and DLC coated glass. From these curves it can be noted that the loss of material with time is significantly lower for the DLC coated glass. In the same figure, additional lines have been shown indicating what could have been the wear loss if wear were linear in time. It is clear that the weight loss of the material in both the cases increases with time sublinearly. This type of sublinearity can be explained with the help of figure 2 as follows. As shown in figure 2a at time $t=0$, the ball is in touch with the sample surface with the force of $F=50\text{ g} \times 980\text{ cm/sec}^2$ acting over the contact area A_0 . The local pressure applied on the sample surface then becomes $P=F/A_0$. Now at time $t=t_1$, the ball penetrates vertically through some distance and the effective contact area under the ball becomes more as shown in figure 2b. Since the load is constant throughout the experiment, as the contact area increases the effective local pressure due to sliding ball decreases, causing low weight loss of material at any local point with a time interval. Of

Table 1. Weight loss of DLC coated and uncoated glass samples as a function of time.

Thickness ($\text{\AA}$)	30 $\text{\AA}$	100 $\text{\AA}$	300 $\text{\AA}$	Uncoated
time (h)	Weight loss in μg			
1	20	30	80	400
2	50	62	98	—
3	90	120	132	972
4	116	—	200	—
5	—	—	378	2290

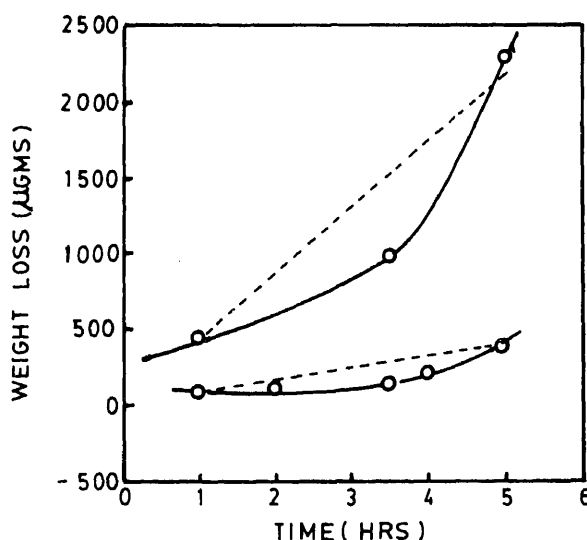


Figure 1. Weight loss of material as a function of time.

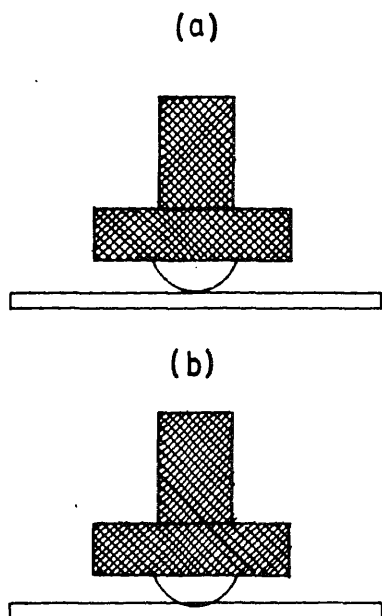


Figure 2. Geometry of sliding ball with respect to (a) at time $t=0$, ball is in contact with sample surface of area A_0 and (b) at time $t=t_1$, ball is in contact with sample surface with wear area A_1 ($A_1 > A_0$).

course, the total area over which the loss occurs increases and hence we have a product of a decreasing function and an increasing one. The sublinearity shows that the decreasing function operates more efficiently.

The amount of wear was also determined by microscopic examination of the wear scar using an optical microscope. Figures 3a and b show optical micrographs of the uncoated glass and 300 Å DLC coated glass, respectively. No specific differences in the surface features can be observed. Figure 4a shows the optical micrograph of the uncoated glass for a wear time (viz. the time for which the sample is rotated at a speed of 300 rpm with a load of 50 g) of 1 h and figure 4b shows the optical micrograph of the DLC coated glass for the same wear time. These two photographs together indicate that the wear scar in the case of the uncoated sample is significantly prominent than the DLC coated sample. In the case of DLC coated sample there is only slight appearance of a line with very low contrast with respect to the coated surface. Figure 5a shows the optical micrograph for the uncoated glass for a wear time of 3 h and figure 5b shows the optical micrograph of DLC coated glass sample for the same wear time. In these photographs also we observe major wear scar in the case of uncoated sample whereas there are only tiny scratches on the DLC coated surface. These observations and comparison of the wear scars in case of uncoated and coated samples clearly indicate major improvement in the mechanical surface properties of glass due to DLC coating.

To study the optical properties, different glass/quartz samples were coated with DLC of varying thicknesses in the range 30 Å to 300 Å. Transmission and reflection

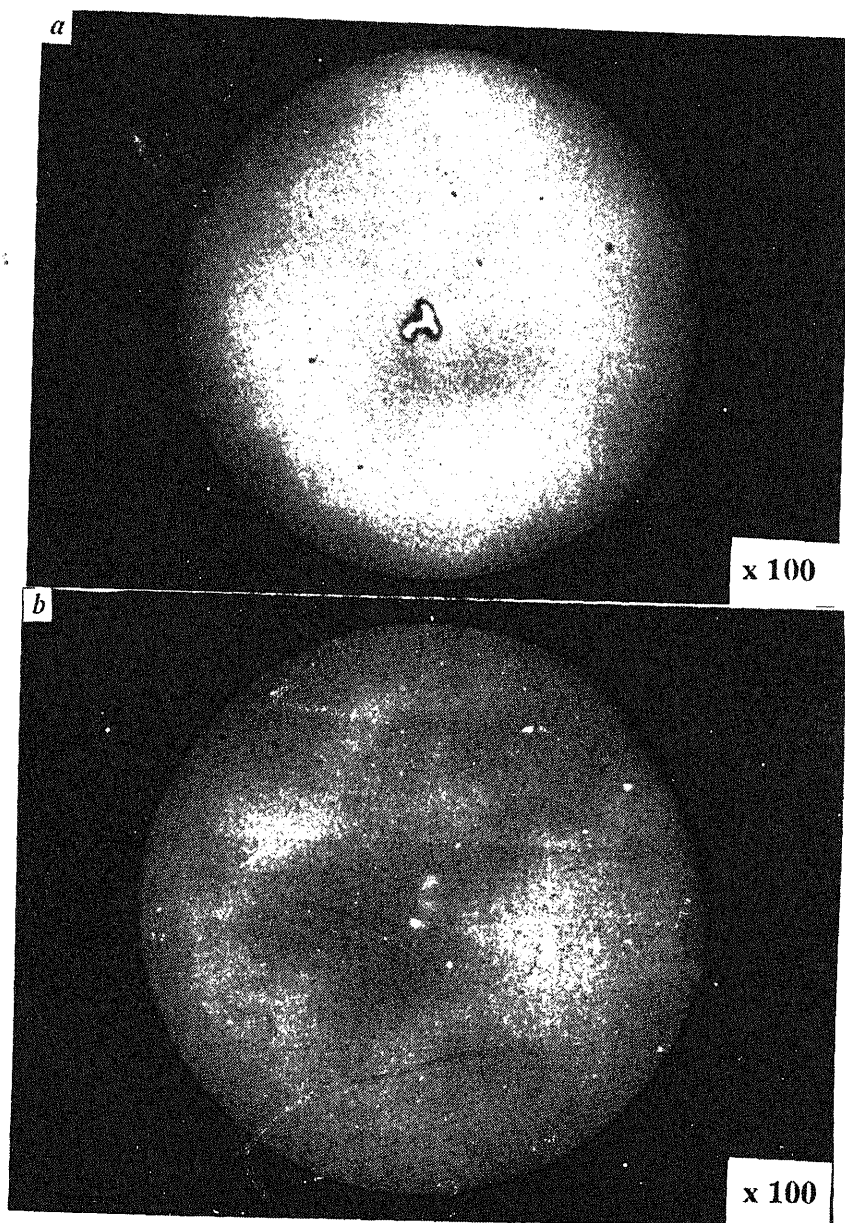


Figure 3. Optical micrograph of (a) uncoated glass and (b) 300 Å DLC coated glass.

spectra were acquired with a Perkin-Elmer Lambda spectrophotometer. This instrument was used in double-beam transmission and reflection mode. Figures 6 and 7 are the plots of transmission (T) and reflection (R) (in%) vs thickness for different wavelengths in the visible range. For lower thicknesses we observe that T and R do not vary much with wavelength. Also, transmittivity of DLC decreases whereas

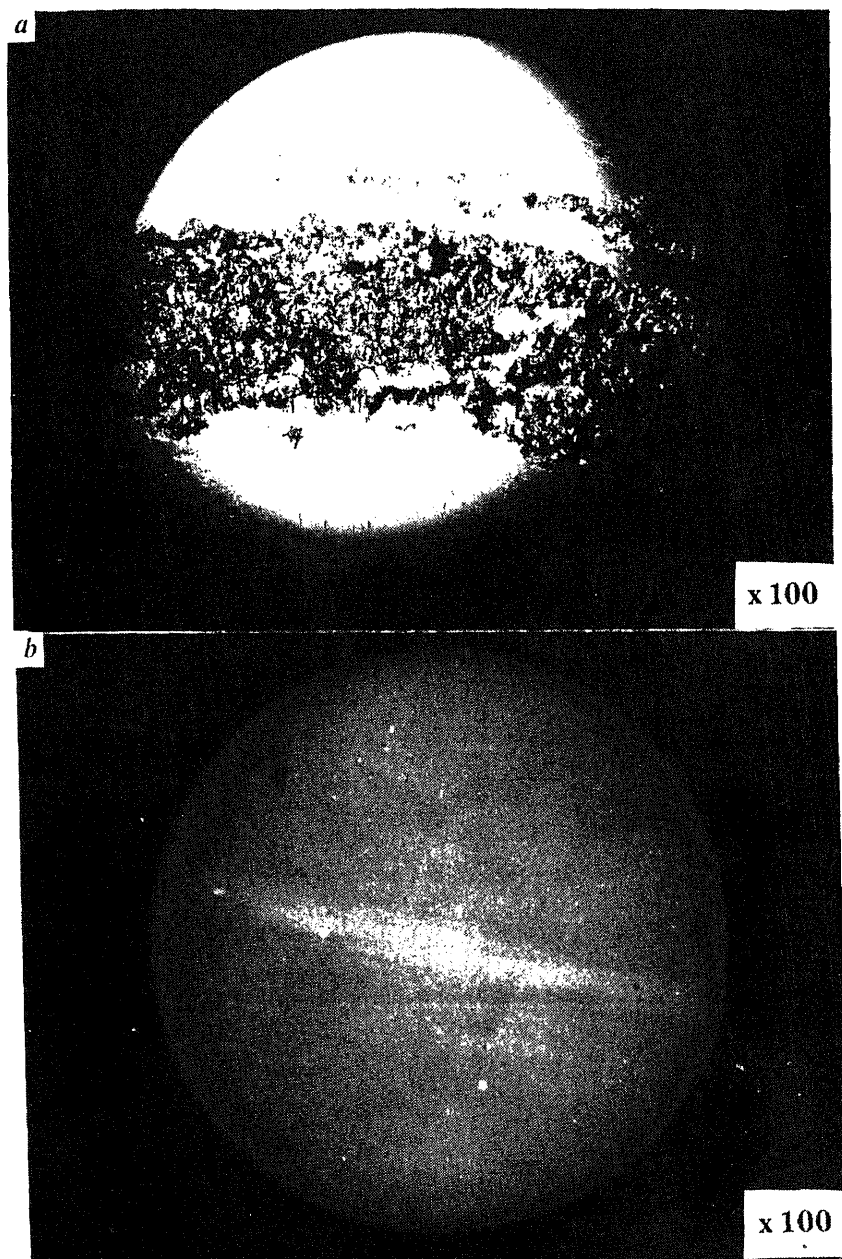


Figure 4. Optical micrograph of 1 h wear tested sample of (a) uncoated float glass and (b) 300 Å DLC coated float glass.

reflectivity increases with increasing film thickness. The optical band gap of DLC film was obtained from the Tauc relation,

$$(\alpha E)^{1/2} = B(E - E_g),$$

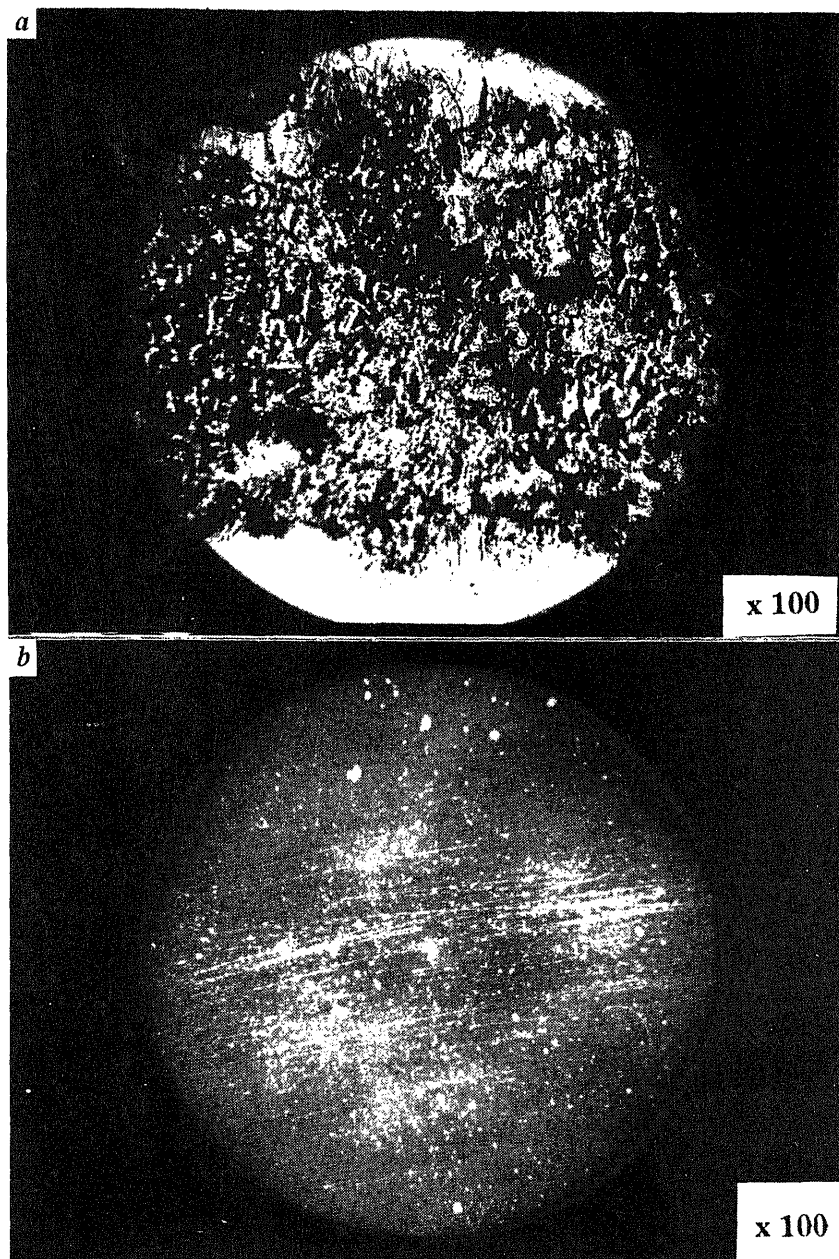


Figure 5. Optical micrograph of 3 h wear tested sample of (a) uncoated float glass and (b) 300 Å DLC coated float glass.

where α is the absorption coefficient, E the energy, B a constant and E_g the optical gap. The Tauc plot for the case of 100 Å DLC coated on quartz is shown in figure 8 and the optical band gap turns out to be 1.4 eV.

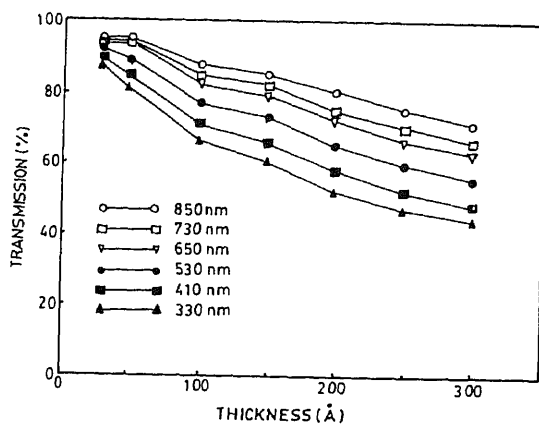


Figure 6. Plot of transmission (T) in % vs thickness of DLC for different wavelengths of light in the visible region.

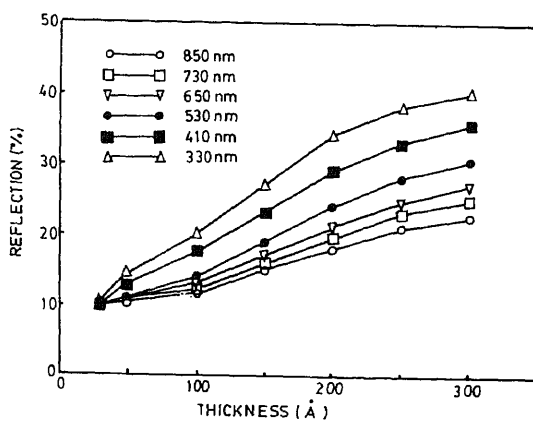


Figure 7. Plot of reflection (R) in % vs thickness of DLC for different wavelengths of light in the visible region.

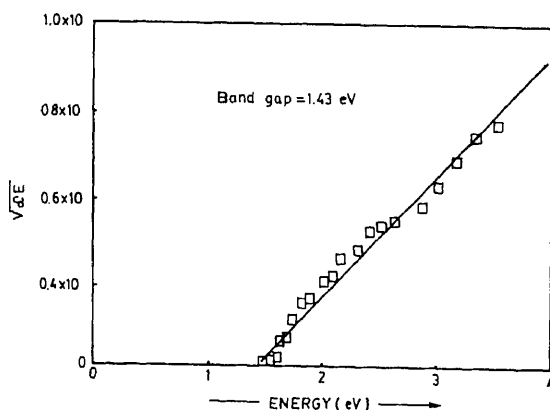


Figure 8. Tauc plot of energy E in eV vs $(\alpha E)^{1/2}$ for 100 Å DLC on quartz.

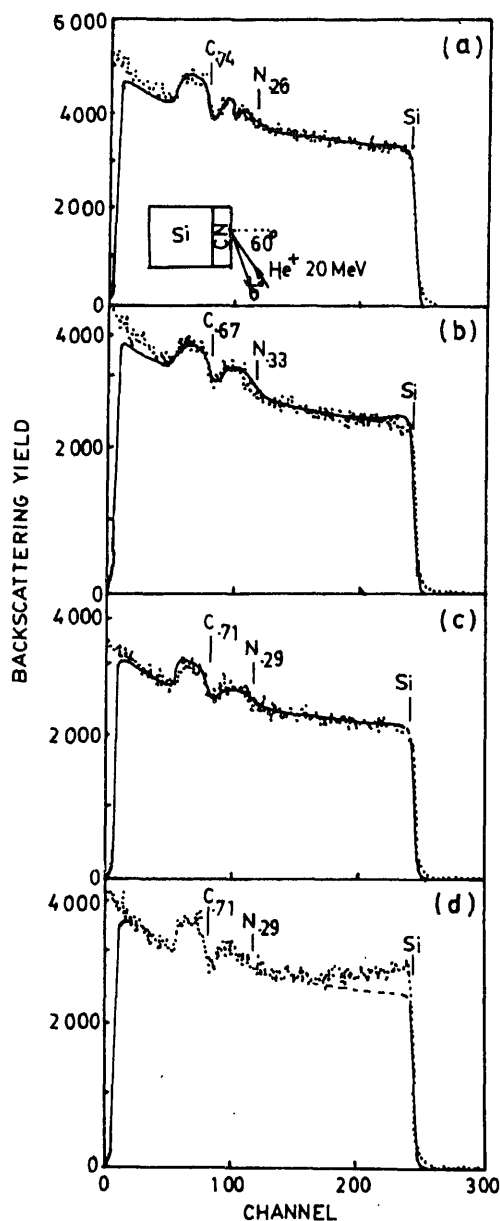


Figure 9. Rutherford backscattering spectra of C-N films deposited at substrate temperature of (a) 200°C, (b) 300°C, (c) 400°C and (d) 500°C.

From table 1 (or figure 1) the weight loss for uncoated glass for 1 h sliding is 400 µg whereas the weight loss for DLC coated glass samples having DLC thicknesses of 30 Å, 100 Å and 300 Å is 20, 30 and 80 µg, respectively. This clearly indicates a significant improvement in the mechanical surface properties of

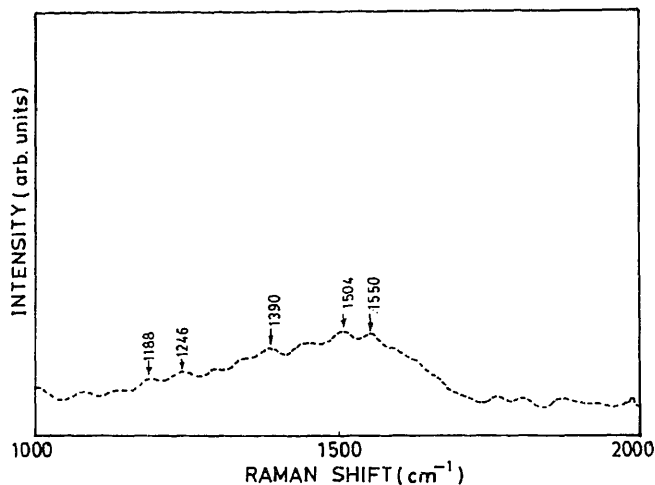


Figure 10. Laser Raman spectrum of C-N film on Si (100) substrate with 33% nitrogen.

glass by DLC coating. Interestingly, the 30 Å film shows superior wear features as compared to the 100 Å and 300 Å films. This should reflect a higher diamond like character of a thinner film as compared to the thicker one. In the initial phase of growth, the mechanism would involve growth of DLC on glass while in the latter phase, DLC on DLC. It appears that growth of DLC on DLC progressively degrades its quality. Detailed Raman and IR reflectance studies are in progress to understand these aspects of growth.

3.2 C-N films

For the deposition of C-N films on Si(100) using IBAAD technique we chose the nitrogen ion energy and current to be 300 eV and 40 mA respectively and varied the substrate temperature from 200–500°C. Carbon evaporation rate was maintained at 1 Å/sec. These parameters were so chosen that the number of ions arriving at the substrate/cm²/sec was 1.33 times the number of evaporating carbon atoms/cm²/sec for achieving C₃N₄ stoichiometry. These films were characterized using RBS in order to determine chemical composition of the C-N films. Figures 9a–d show the RBS data for the films deposited at the substrate temperatures of 200°C, 300°C, 400°C and 500°C. The atomic percentage of nitrogen in these cases is 26%, 33%, 29% and 29%, respectively. For C₃N₄, there should be 57% nitrogen ideally whereas we get maximum nitrogen incorporation of 33% only. Further investigations are in progress for increasing the nitrogen content in C-N films using this technique. The representative Raman spectrum of C-N film with 33% nitrogen is shown in figure 10. This spectrum shows a broad hump between 1100 and 1700 cm⁻¹ with features near 1390 cm⁻¹ (D peak) and 1550 cm⁻¹ (G peak) similar to those of DLC. The features near 1200 cm⁻¹ and 1500 cm⁻¹ correspond to vibrational modes of linear C-N bonds. All the spectral features are in general agreement with the C-N Raman spectra reported in literature for films obtained by other techniques (Chen *et al* 1993).

4. Conclusions

Tribological properties studied by subjecting DLC coated films to the accelerated wear tests confirmed a significant improvement in the mechanical surface properties of glass by DLC coating. We obtained better wear features for thinner DLC coatings as compared to the thicker ones. From the study of optical properties we obtained a band gap of 1.4 eV of DLC films. C-N films prepared using IBAD technique indicated a maximum of 33% nitrogen only. Variation in the nitrogen content in the C-N film with substrate temperature was observed.

Acknowledgements

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Creation of nanostructures on nickel thin films by STM

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Abstract. A scanning tunneling microscope (STM) has been used to create nanostructures on nickel thin films. A systematic procedure for the creation of such structures has been developed. Various possible mechanisms involved in such creations have been discussed. Based on our observations, a field-induced suction of the plastically deformed surface has been proposed.

Keywords. Nickel; thin film, nanostructures; STM.

1. Introduction

One of the subjects of great current interest in scanning tunneling microscopy (STM) is its application in the manipulation of atoms and molecules on solid surfaces (Becker *et al* 1987; Rohrer 1993) and in creating lithographic structures on a nanoscale. The possibility of creation of structures such as quantum wires and quantum dots of highly specific dimensions at specified locations on a nanometre scale has opened up an exciting frontier in surface science and technology. Various surface modification techniques using STM are described as nanomachining (Virtanen *et al* 1991), nanoindentation (Schmmele *et al* 1992), nanoetching (Saulys *et al* 1991), nanostructuring using high field (Snow *et al* 1993), high current (Hartmann *et al* 1991), and pulse (Schmmele *et al* 1991), and nanolithography (McCord and Pease 1988). McCord and Pease (1986, 1987) have written 200-nm-wide lines on thin resist films using STM. Stauffer *et al* (1987, 1988) created small hillocks of ~35 nm diameter by locally melting a glassy substrate. It has been shown by Schneir *et al* (1988) that 5-nm-wide lines can be written if the substrate is first covered by a fluorocarbon grease.

Fabrication of nanostructures on surfaces using STM can be attained either by tip-sample direct indentation, or by interaction at a distance between the two. In the former method, modification of the solid surface is usually achieved by locally destroying the surface, i.e. mechanically scratching the surface with the tip (Schneir *et al* 1988). In this process the tip loses its sharpness, thereby making it ineffective for subsequent topographic application. The other technique, which is referred to as tip bias pulsing method, is essentially a nondestructive method. In this technique, the main control parameters for 'writing pulse' are the sign, magnitude, duration and number of voltage pulses applied between the tip and the sample. Using this method one can create either valleys (Li *et al* 1989) or hillocks (Mamin *et al* 1990). However, it has been observed that the shape of the created structure depends not only on the tip shape but also on the nature of the sample surface. In bias pulsing technique, the STM is operated in field emission mode for a very limited time. Recently there have been a series of investigations on gold as it is known to have a lower threshold for field evaporation compared to refractive metals. It

has been pointed out that tip-sample direct interaction is also possible in the bias pulse technique (Pascual *et al* 1993). These coupled interactions may lead to structures completely different from what we expect. However, the real physical mechanism underlying this phenomenon is not well understood.

In the present investigation we have attempted to develop a procedure to use bias pulsing technique to create and modify nanometric structures on nickel thin films. We also discuss the possible physical mechanism underlying this phenomenon.

2. Experimental

Thin films of nickel of various thicknesses on different substrates were deposited using electron beam evaporation technique under high-vacuum conditions (10^{-7} torr). The samples were subsequently transferred to STM chamber, where these experiments were carried out in air. Electrochemically etched sharp tungsten tips (Rao and Mathur 1993) were used for topographic scan with 0.25 V bias voltage and 200 pA tunneling current in constant current mode. The bias pulsing method used in the present work for creation of nanostructures was done in the constant height configuration. This procedure has been followed in order to avoid tip-sample direct interaction. A digital storage oscilloscope was used to record pulse height and width precisely.

Prior to the surface modification, smooth areas were selected by scanning large areas at different locations on the sample surface. The average surface roughness was found to be 15–25 Å. These scans were also taken in order to make sure no structures were present prior to the surface modification. After the topographic scan with constant current configuration the tip was moved to a particular location where the surface modification was desired. Then we switched over to the constant height mode and subsequently the voltage pulse was directly added to the tunneling voltage.

The positioning of the tip, the shape of the tip and the shape of the pulse are important parameters governing nanostructuring. In our STM, the sample is mounted on a piezo tube and the position of the sample below the tip can be adjusted by controlling the voltage applied to the offset piezo. This facility permits us to shift the sample in a precisely controlled manner so as to position the tip at the required location on the surface.

The shape of the nanostructures is not an exact replica of the tip shape but is greatly influenced by it. Trials with various grounded tips produced different structures. As an example, the triple structures seen in figure 1 are most probably due to a tip having three pointed corners at different heights. In the imaging mode, the pointed corner closest to the surface is the main contributor to the tunneling current. But in the high-field mode, the three points of the tip generate different fields on the surface, thereby creating three hillocks of different sizes. This has been checked at three different locations and we see that hillock structures are similar. In order to produce small symmetrical structures, it is desirable to use a tip which is pretested on standard sample for atomic resolution.

The voltage amplitude and width of the pulse necessary to produce nanostructures depend on the material of the surface. Earlier workers have reported voltage pulse widths in the range of a few microseconds to a few milliseconds for different

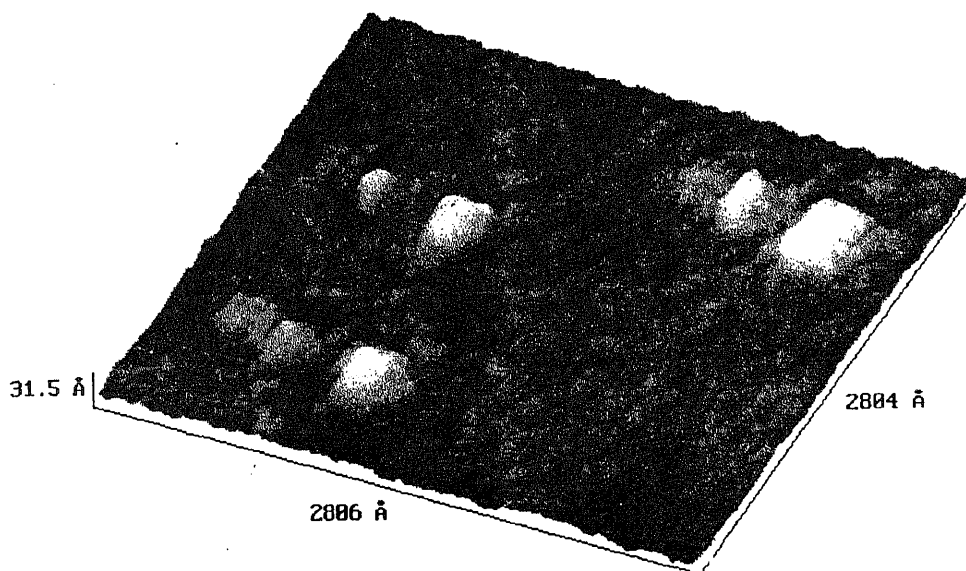


Figure 1. Nanostructures created by a triple-pointed tip at three different locations.

materials. Our trials show that for production of stable plastic deformation on the surface of nickel film on mica, a 100-ms-wide pulse is sufficient. It is found that the structure could be created only with a certain minimum pulse height for a specified tip-sample distance. We observed that the writing probability goes from 0 to 100% within a fraction of a volt and this voltage is determined by repeating the experiment several times. The threshold voltage for nickel was found to be 2.5 V when the tunneling conditions just before writing were $V=0.25$ V and $I=200$ pA, below which there is no surface modification. At 2.5 V, formation of hillocks commences of height ~ 50 Å and diameter ~ 200 Å. As the voltage increases, the overall size increases but the shape remains more or less the same. The inner two hillocks in figure 2, were formed with a bias pulse of 3.0 V whereas the outer ones were created by a 4.0 V pulse. It is seen that the hillocks created by 4.0 V pulse are larger than those created by 3.0 V pulse but the overall shape remains more or less the same. A similar behaviour as seen in figures 1 and 2 has been observed in a large number of trials. The observations suggest that the shape of the hillock is governed by the shape of the tip but the overall size is determined by the effective field strength on the surface. A pulse greater than 4.5 V produces drastic changes in the surface topography.

A single-parameter quantification of surface modification is desirable. This involves measurement of physical dimensions of the nanostructures. Although it is possible to measure these dimensions using image processing techniques this only generates a large amount of data. Fractal characterization in terms of scaling exponent is difficult to recommend because the surface can no longer be regarded as self-affine due to area-specific modifications. In order to standardize the nano-structuring procedure, it is necessary to use a parameter which defines the extent of modification.

As the structures produced during our investigations are in the shape of hillocks, a rough estimate of their volume is used in our investigations to characterize the nanostructures.

As the bias pulse amplitude increases, the volume of the nanostructures also increases. Figure 3 is one such plot characterizing the surface modification with

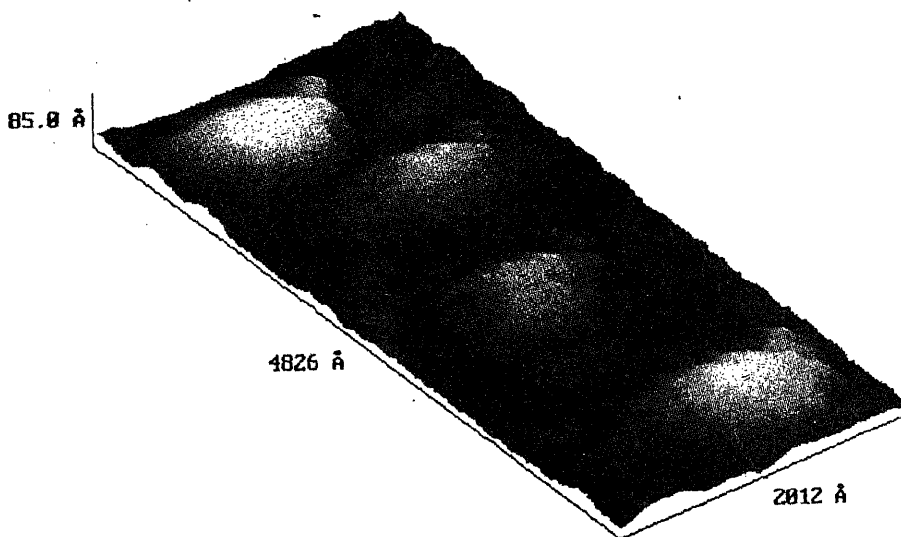


Figure 2. Nanostructures created using the same tip. The outer two were created using a voltage pulse of height 4.0 V, whereas the inner ones are with 3.0 V.

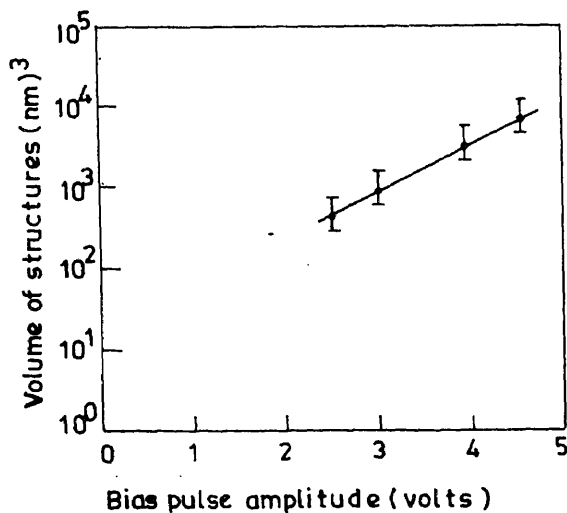


Figure 3. Characterization of nanostructures created on nickel thin film by bias pulse method.

spect to the voltage of the bias pulse using a sharp tungsten tip. For voltage less than 2.5 V there is no surface modification whereas voltage above 4.5 produces plastic changes in the surface morphology. It is to be noted that the line plot may drift up or down by as much as 50% depending on the shape of the tip.

The following procedure was followed to form a single hillock using a sharp tip and a line of broad hillocks using a broad tip. After the topographic scan with constant current configuration (figure 4a) the tip was moved to the central location where the surface modification was desired. Then we switched over to the constant voltage mode and subsequently the voltage pulse was directly added to the tunneling voltage. The amplitude and width of the pulse recorded by digital storage oscilloscope were noted to be 4.5 V and 100 ms respectively. The transient electric field, which was created by bias pulse method, was sufficiently high to obtain plastic instead of purely elastic deformation of the surface. After the application of bias pulse the

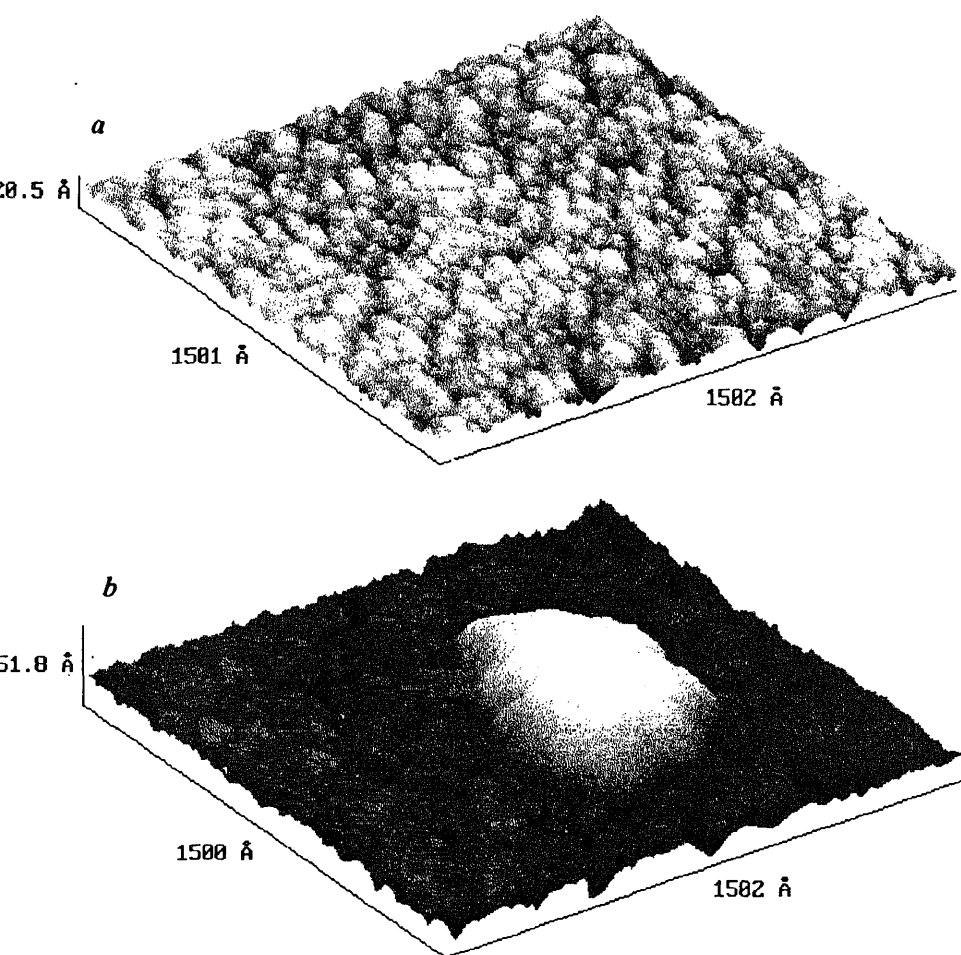


Figure 4. Formation of nanostructure by bias-pulse method (a) before and (b) after application of 2.5 V pulse of 100 ms width on nickel film.

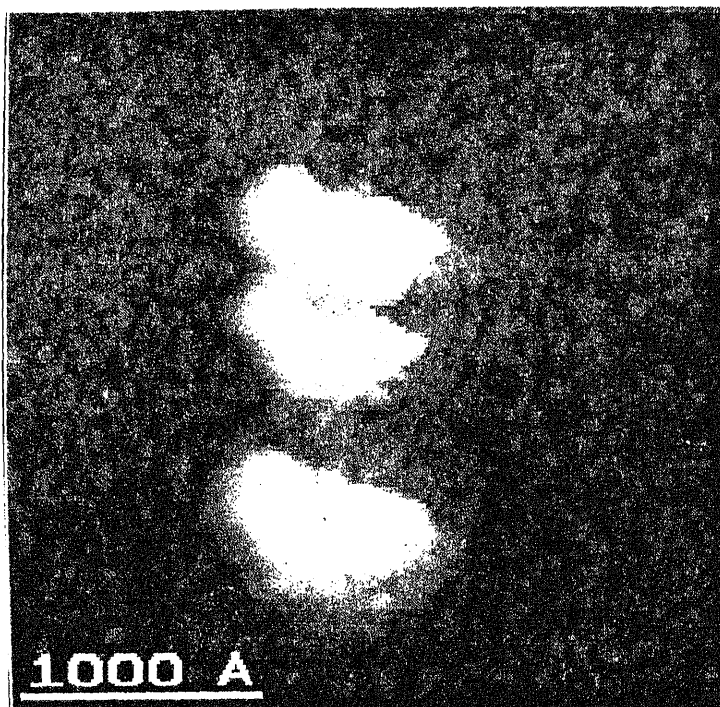
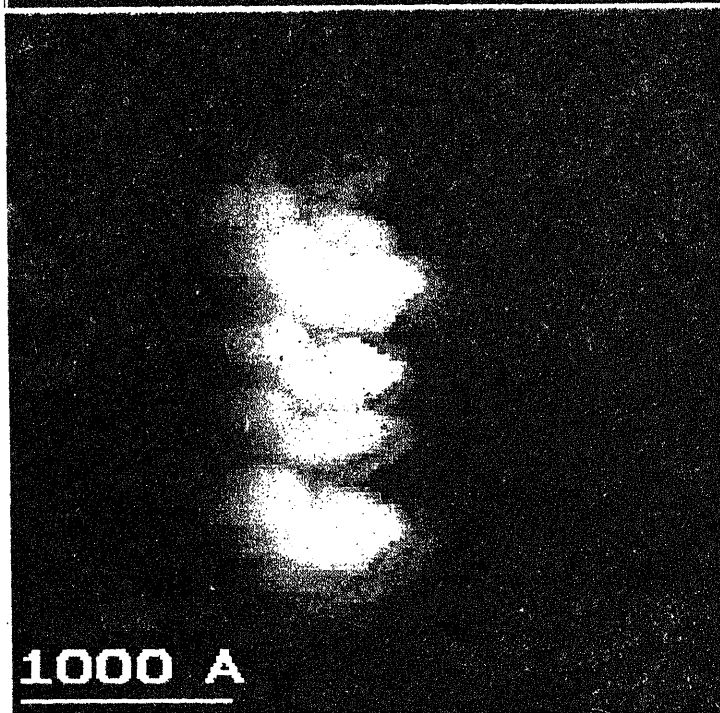
a*b*

Figure 5. Creation of a line pattern by repeated application of bias pulse at different locations. Note that the discontinuity of **a** has been removed in **b** by precisely positioning the tip at the proper location.

STM was switched back to constant current mode and the topographic image was recorded (figure 4b). It is clearly seen that a mound of 50 nm diameter and 5 nm height is created.

In order to draw a line, it is necessary to create a number of structures along the line. As the offset controls permitted us to steer the sample to bring the desired location just below the tip, we could create the line. In figure 5a, the bias pulse signal could not reach the tip at one location, causing a discontinuity of the line. However, the structure was further modified by precisely positioning the tip in between two hillocks so as to complete the line (figure 5b). The interesting aspect revealed by figures 5 a and b is the precision of control in positioning the tip which is very crucial for writing a continuous nanostructure.

3. Results and discussion

The formation of hillocks is a matter of debate. When the experiments were performed on a gold surface with a gold tip (Mamin *et al* 1990) it was first proposed that material from the tip was getting field-evaporated and deposited on the substrate. This theory was contested by Pascual *et al* (1993) who argued that the formation is due to instantaneous mechanical contact between tip and sample. Tsong (1991) reviewed the various possible tip-sample atomic interactions that are possible in the field emission mode in a STM. He suggests that depending on the threshold fields for field evaporation for the tip and sample material, either of them may evaporate. In our present investigation we have used a tungsten tip for modifying nickel thin-film surfaces. We observed that even after repeated use of

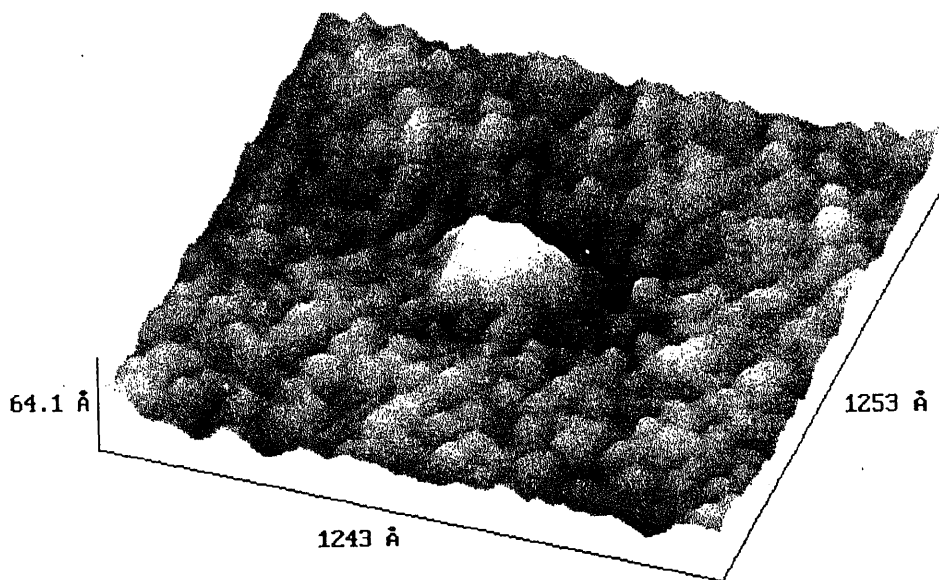


Figure 6. Formation of valley just adjacent to the hillock created by bias pulse method.

the tip in field application mode, the quality of the STM images scanned with the same tip did not deteriorate. Secondly, as such, the movement of the tip was frozen during field application and there was no 'short circuit' between the tip and the sample and therefore the mechanical contact model (Pascual *et al* 1993) could not be supported. The transient electric field which is created by bias pulse method can be sufficiently high to obtain plastic instead of purely elastic deformation of the surface, in which case the mound formation can be attributed to, first, local melting and plastic deformation of film material and then its suction towards the tip by a high field gradient. The topograph in figure 6 clearly shows the existence of a valley just behind the hillock. This valley is likely to have been created during field-induced 'suction' of the surface material. Based on these observations, the 'suction' model of creation of nanostructures appears plausible.

4. Conclusions

Based on our observations, we conclude that nanostructures can be created on nickel thin-film surface by bias pulse technique. The structures are characterized in terms of their volume. It is found that good, reproducible structures could be created with a voltage pulse height in the range of 2.5 to 4.5 V and width 100 ms. The shape of the hillock is governed by the shape of the tip but the overall size is determined by the effective field strength on the surface. The transient electric field created by bias pulse method can be sufficiently high to obtain plastic instead of purely elastic deformation of the surface, in which case the mound formation can be attributed to, first, local melting and plastic deformation of film material and then its suction towards the tip by a high field gradient.

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Synthesis of aluminium matrix composites containing nanocrystalline oxide phases

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Abstract. Using nanocrystalline particles of mullite and zirconia respectively with diameters in the range 20–30 nm prepared by a sol-gel route, aluminium metal-matrix composites have been synthesized. A hot pressing technique has been used with temperatures varying from 450–610°C. The vickers hardness values for the composites are found to be substantially higher than that of pure aluminium. An order of magnitude increase in hardness is achieved when Al_3Mo phase is grown in the composite.

Keywords. Nanocrystalline; mullite; zirconia; aluminium; composites.

1. Introduction

Aluminium-based metal-matrix composites have received increasing attention in recent years for potential applications in structural parts (Marsden 1985; Ohtsu 1989) and engine components (Flinn 1990; Lampman 1991). In most of the investigations reported, improvement of mechanical properties has been studied in systems consisting of ceramic particulates or whiskers dispersed in an aluminium matrix (Lee and Subramanian 1993; Pandey *et al* 1993). In all the work referred to above the size of the ceramic particles has been of the order of a few micrometers. We have prepared aluminium based metal-matrix composites containing nanometer sized particles of mullite and zirconia respectively. To our knowledge synthesis of such composites has not been reported earlier. We have carried out hardness measurements on the synthesized samples. A marked increase in the hardness value has been observed in specimens containing nanocrystalline oxides as compared to that of pure aluminium. The preliminary results are described in this paper.

2. Experimental

Nanocrystalline mullite was prepared by a sol-gel method. The starting materials were AR grade $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Si}(\text{OC}_2\text{H}_5)_4$ of appropriate amounts. The gel powder obtained from the precursor sol was hot pressed in a DSP 25 ATS Sintering Press (manufactured by M/s Dr Fritsch Sondermaschinen, Germany) at a temperature of 750°C for 5 min under a pressure of 24 bar. The details of synthesis have been reported earlier (Pradhan *et al* 1994). For the synthesis of nanocrystalline zirconia the starting material was $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. To a solution of the latter distilled water aqueous ammonia was added dropwise to bring about a complete precipitation of $\text{Zr}(\text{OH})_4$. By suitable heat treatment of the filtered mass nanocrystalline ZrO_2 ,

comprising of cubic, tetragonal and monoclinic phases, respectively were obtained. The details are reported elsewhere (Chatterjee *et al* 1994).

For preparation of the aluminium metal matrix composites in the present investigation the required amount of commercial grade aluminium powder (of 99.7% purity) was mixed with ~23 volume% of the oxide particulates viz. ZrO_2 and mullite, respectively synthesized as described in the previous section. The volume fraction of the ceramic phase as mentioned above was chosen because optimum mechanical properties were reported in literature for conventional metal matrix composites for this value (Patnolli and Zaffanini 1991). The mixture consisting of aluminium metal and ceramic powders was ground in a mortar under acetone for about 2 h. The mixture was then subjected to vigorous stirring in an ultrasonic bath. The mixed powder was then taken in a graphite mould. The latter was mounted in a DSP 25 ATS Sintering Press supplied by M/s Dr Fritsch Sondermaschinen, Germany. The pressing was done in an evacuated chamber with a pressure of 0.26 bar at temperatures varying from 450–610°C with an applied pressure of 24 bar for a duration of 2 min. Some specimens were also prepared by covering the mixed powder of aluminium and nanocrystalline oxide with molybdenum foils with a thickness of ~25 μm during the hot pressing operation.

The various crystalline phases in the composites synthesized were determined from the X-ray diffractograms taken in a Phillips X-ray diffractometer (PW 1710) using CuK_α radiation. The particle sizes of the different phases were determined using Scherrer equation (Klug and Alexander 1974). We have used pure aluminium as instrumental standard. Step scan data of instrumental and sample profiles were fitted analytically using pseudo-Voigt function and full width at half maxima (FWHM) was estimated after complete peak separation for at least first four reflections of aluminium (Enzo *et al* 1988). In our samples the particle size of aluminium was found to be ~1.5 μm . The sizes of mullite and zirconia particles were estimated to be 20 nm and 29 nm respectively. The microhardness of the specimens prepared after polishing the surface with 1 μm diamond paste was investigated by the Vickers microhardness tester (model mph 160) attached to a high resolution optical microscope (Carl Zeiss Jenavert) with a DIK attachment. The indentations were carried out at a given load and the Vickers hardness H_v was obtained from the relation

$$H_v = 1.8544 \frac{P}{d^2}, \quad (1)$$

where P is the applied load in kilograms and d the diagonal measure of indentation in mm.

3. Results and discussion

Figure 1 shows the X-ray diffractograms of the different composites prepared in this work. It is evident that samples 1 to 6 contain $\alpha\text{-Al}_2\text{O}_3$ besides the mullite phase. Also, for the sample hot pressed at 610°C with a molybdenum foil covering the starting mixture of aluminium and the oxide phase, the growth of the intermetallic phase Al_5Mo takes place. Such low temperature formation of Al_5Mo is ascribed to an increase in kinetics for the formation of this phase at high pressure. For samples

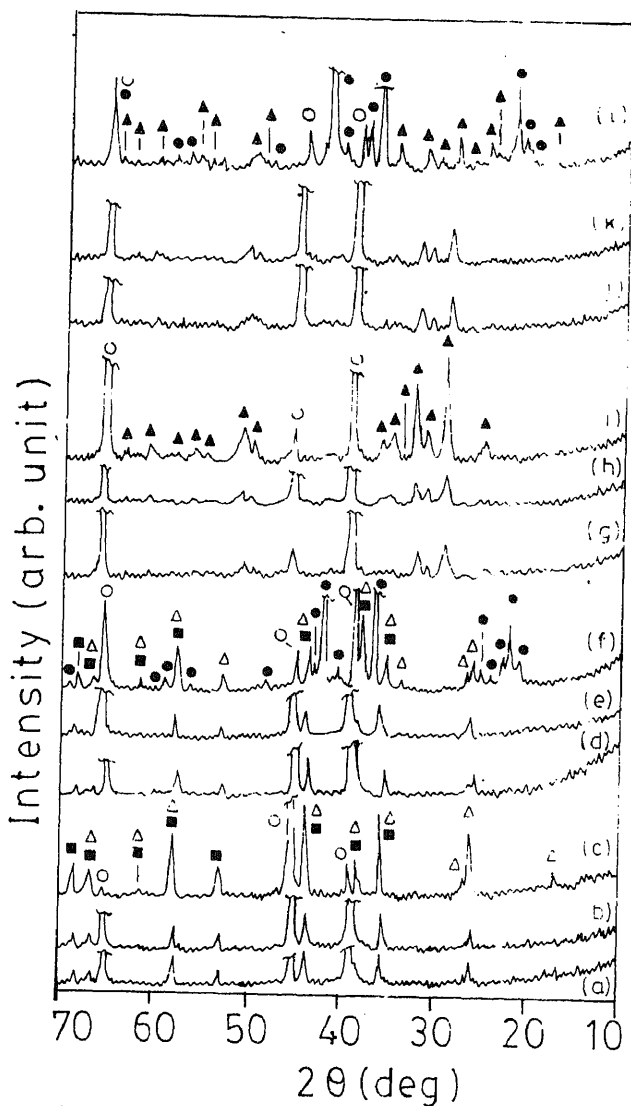


Figure 1. X-ray diffractograms of different aluminium matrix composites: (a) Al + mullite hot pressed at 450°C, (h) Al + mullite hot pressed at 550°C, (c) Al + mullite hot pressed at 610°C, (d) Al + mullite hot pressed between molybdenum sheets at 450°C, (e) Al + mullite hot pressed between molybdenum sheets at 550°C, (f) Al + mullite hot pressed between molybdenum sheets at 610°C, (g) Al + ZrO₂ hot pressed at 450°C, (h) Al + ZrO₂ hot pressed at 550°C, (i) Al + ZrO₂ hot pressed at 610°C, (j) Al + ZrO₂ hot pressed between molybdenum sheets at 450°C, (k) Al + ZrO₂ hot pressed between molybdenum sheets at 550°C, (l) Al + ZrO₂ hot pressed between molybdenum sheets at 610°C. (○, Al; ■, α -Al₂O₃; Δ, mullite; ●, Al₃Mo; ▲, ZrO₂).

7 to 12 it is obvious that ZrO₂ exists in cubic, tetragonal and monoclinic phases. Also at 610°C in this sample series Al₃Mo forms at 610°C under high pressure conditions.

Table 1 summarizes the Vickers hardness values obtained in the case of different

Table 1. Summary of Vickers hardness in different composites containing nanocrystalline oxide phases.

Specimen no	Hot pressing temperature (°C)	Phases present in the composite	Vickers hardness (H_v) (kg/mm ²)
1	450	Al, mullite, α -Al ₂ O ₃	22
2	550	"	25
3	610	"	59
4	450 (with Mo sheet)	"	23
5	550 (with Mo sheet)	"	26
6	610 (with Mo sheet)	Al, Al ₅ Mo, mullite, α -Al ₂ O ₃	184
7	450	Al, ZrO ₂ (Cubic + tetragonal + monoclinic)	43
8	550	"	45
9	610	"	72
10	450 (with Mo sheet)	"	43
11	550 (with Mo sheet)	"	49
12	610 (with Mo sheet)	Al, ZrO ₂ (Cubic + tetragonal + monoclinic), Al ₅ Mo	215

composite systems. The H_v value for pure aluminium was measured to be equal to 14 kg/mm². It is evident from the results shown in table 1 that the hardness value increases by a factor of 4 to 5 when the nanocrystalline dispersoids of mullite or zirconia are present in the aluminium matrix and the hot pressing is carried out at a temperature of 610°C. For treatment temperature in the range 450–550°C the increase is by a factor 1.8–3. It is interesting to note that the hardness increases drastically when the Al₅Mo phase is formed at 610°C under high pressure due to the presence of molybdenum sheet cover on the starting powder mixture. In the latter case the hardness increases by more than an order of magnitude.

The remarkable improvement in hardness of aluminium metal matrix composites containing either mullite or zirconia dispersoids with nanometer dimensions may be due to the pinning of dislocations between closely spaced particles of the oxide phase. A detailed examination of the physical mechanism will be reported elsewhere.

In summary, aluminium metal matrix composites containing sol-gel synthesized nanocrystalline oxide particles have been prepared by a hot pressing technique. The Vickers hardness values for these specimens are substantially higher than that of pure aluminium.

Acknowledgement

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Synthesis and properties of zirconia thin films

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Abstract. Thin films of zirconia have been synthesized using reactive DC magnetron sputtering. It has been found that films with good optical constants, high refractive index (1.9 at 600 nm) and low extinction coefficient can be prepared at ambient temperatures. The optical constants and band gap and hence the composition are dependent on the deposition parameters such as target power, rate of deposition and oxygen background pressure. Thermal annealing of the films revealed that the films showed optical and crystalline inhomogeneity and also large variations in optical constants.

Keywords. Magnetron sputtering; zirconia.

1. Introduction

The low temperature synthesis of technologically useful materials in thin film form has been the subject of considerable interest in recent times. This not only enhances applicability of preparation processes but also that of the materials prepared using these processes. Plasma based thin film deposition processes such as sputtering, ion plating etc have traditionally found use in processing of such materials because they allow lower processing temperatures as a consequence of energetic particle bombardment during synthesis. Reactive magnetron sputtering, due to its high deposition rate, reduces target oxidation and offers better control over film composition. Since energetic bombardment of substrates is low, the substrate temperature rise during processing is low. It has, thus, been used successfully to prepare a number of oxides such as titania and zirconia in thin film form at low temperatures. The process has been discussed in detail in recent reviews (Westwood 1989) and hence will not be done here.

Zirconia films are ideal for various technologically important applications because of their durability, hardness, low thermal conductivity, high refractive index, low optical losses etc (Martin *et al* 1983). Since it exhibits polymorphic behaviour, each crystalline modification of zirconia, i.e. monoclinic, tetragonal and cubic, has found application in various areas.

Thus, it is of great interest and importance to prepare and characterize thin films of zirconia. To this end, in this paper we report the preparation of zirconia thin films using DC magnetron sputtering, the optical and structural properties of the films so deposited will also be reported. A study of the thermal stability of these films in respect of optical and structural properties will also be reported.

2. Experimental

The films were prepared in a chamber which was pumped using a diffusion pump (fitted with a liquid nitrogen trap) and rotary pump combination to a pressure of

10^{-6} torr. The target was a 152 mm diameter zirconium plate (99.8% purity). The system was arranged in a sputter up configuration with a target to substrate distance of 65 mm. High purity oxygen (4N) and argon (5N) were used as the reactive and sputter gases respectively.

The target was sputter cleaned for 30 min prior to sputtering. The substrates used were 25 mm diameter fused silica plates. The films were coated to a thickness of 200 nm. The spectral transmittance was recorded in a Hitachi (model 330) spectrophotometer operating in the range 200 to 2500 nm. The refractive indices, extinction coefficient and inhomogeneity in the films were determined using techniques described earlier (Swanpoel 1983; Suhail *et al* 1992). The band gap was calculated from a model proposed by Tauc (1974) for amorphous semiconductors. The X-ray diffraction patterns were recorded in a powder diffractometer using Co-K α radiation ($\lambda = 0.179$ nm).

The films were finally annealed in air over temperature range from 300 to 900°C and characterized for the same properties.

3. Results and discussion

As stated earlier, one of the main advantages of magnetron sputtering is the high rate of deposition (calculated from the total thickness and sputtering time) that it provides. From figure 1a, where the rate of deposition is plotted as a function of target power, it is seen that rates as high as 50 nm/min can be achieved routinely.

The deposition rate as a function of background oxygen pressure has been plotted in figure 1b at a constant target power of 450 W. Initially, as the oxygen pressure is increased the rate of deposition remains constant up to a value of 3×10^{-5} torr, there is a steep drop beyond that and the rate of deposition then becomes constant at and above a pressure of 4×10^{-5} torr. The pressure at which the drop occurs is called the critical oxygen pressure and the drop beyond that point is attributable to target oxidation, because the corresponding oxide will have a lower deposition rate. Blickensderfer *et al* (1976) reported a similar effect during rf sputtering from a Zr target. They have observed a drop from 20 to 4 nm/min at critical pressure of 0.2 mtorr as against the 35 nm/min to 25 nm/min drop observed in the present case. Schiller *et al* (1984) also observed the presence of a critical oxygen pressure during the processing of titania thin films.

The effect of changing pressure and hence the related change in deposition rate on the refractive index of these films (at 600 nm) is shown in figure 2a. The refractive index also appears to be constant up to the critical oxygen pressure but shows a more gradual drop in its value beyond the critical pressure. Further, no saturation is observed in the index value. This clearly indicates that the refractive index is strongly dependent on both the oxygen pressure and the deposition rate (figure 2b) and can be modulated using either of these process parameters thus enhancing the applicability of the process. The values of refractive index obtained, 1.93 at the critical pressure 3×10^{-5} and 1.84 at the highest pressure used in the study 4×10^{-5} torr, are lower than the bulk value of the material (2.21). The value 2.08 obtained at 50 nm/min and the critical pressure however, compares favourably with the bulk value. The low values indicate that the films are porous and probably non stoichiometric. Indirect evidence for stoichiometry is presented in figure 3,

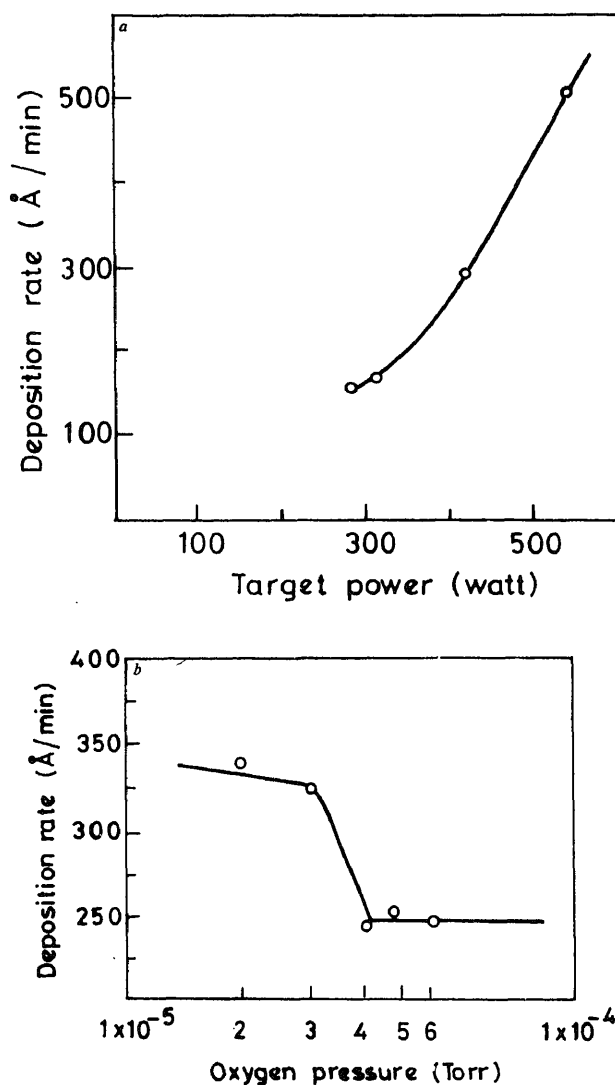


Figure 1. Variation in deposition rate as a function of a. target power and b. oxygen pressure.

where the band gap is plotted as a function of oxygen background pressure. It is seen that as the pressure is increased, initially there is a sharp rise in the optical band gap from 4.7 to 5.1 eV at the critical pressure, 3×10^{-5} torr, and saturates thereafter. This quite clearly indicates that the film composition approaches stoichiometry at this pressure and that further oxygen input does not affect the composition significantly. The highest value of 5.1 eV however, is lower than the bulk value and thus suggests that the films are only nearly stoichiometric and not completely so. This is reflected in the refractive index values also. Demiryont and Sites (1984) had earlier reported that the optical band gap of ion beam sputtered

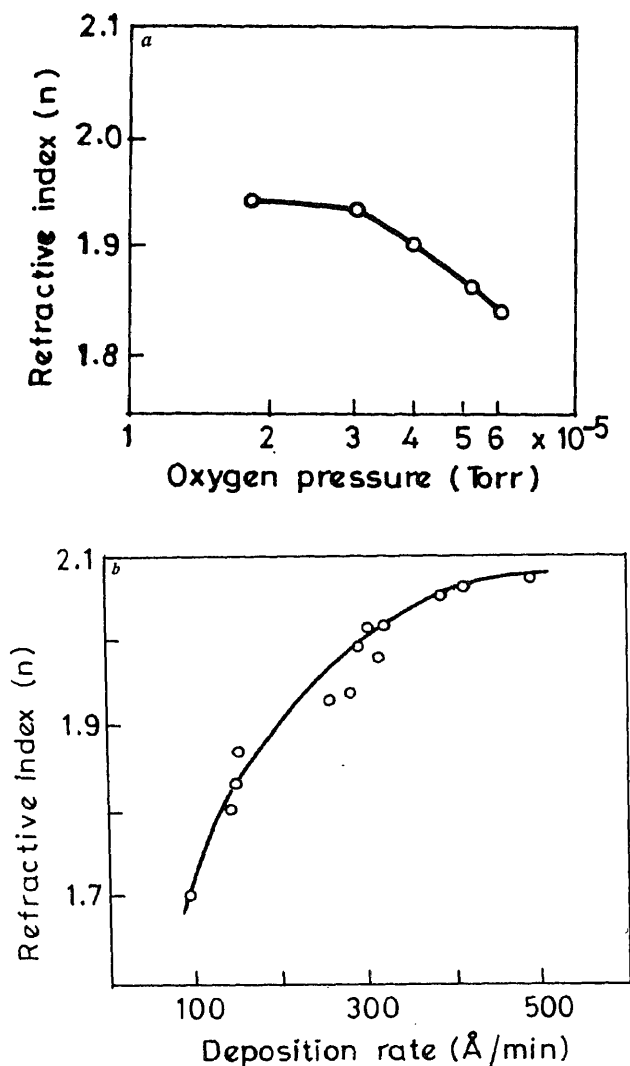


Figure 2. Variation in refractive index as a function of a. oxygen pressure and b. deposition rate.

titania films is a strong function of oxygen content in the films and hence the premise that the films in present case are stoichiometric at the critical oxygen pressure seems justified.

Rutherford backscattering spectroscopy done on samples prepared at 3×10^{-5} torr, indeed show that the films are nearly stoichiometric (figure 4).

Thus, it appears that stoichiometric films of zirconia can be synthesized at low temperatures using magnetron sputtering. Significantly, the observed temperature rise during deposition was not more than 40°C even at the highest power conditions. The reaction therefore, apparently, proceeds by an energetic particle induced diffusion and mixing mechanism. Netterfield *et al* (1988) had earlier reported that in ion

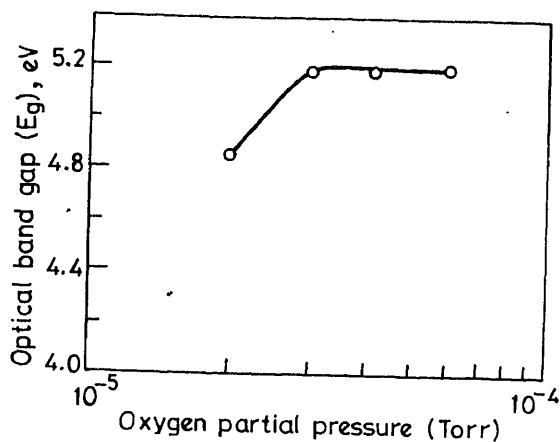


Figure 3. Variation of optical band gap as a function of oxygen pressure.

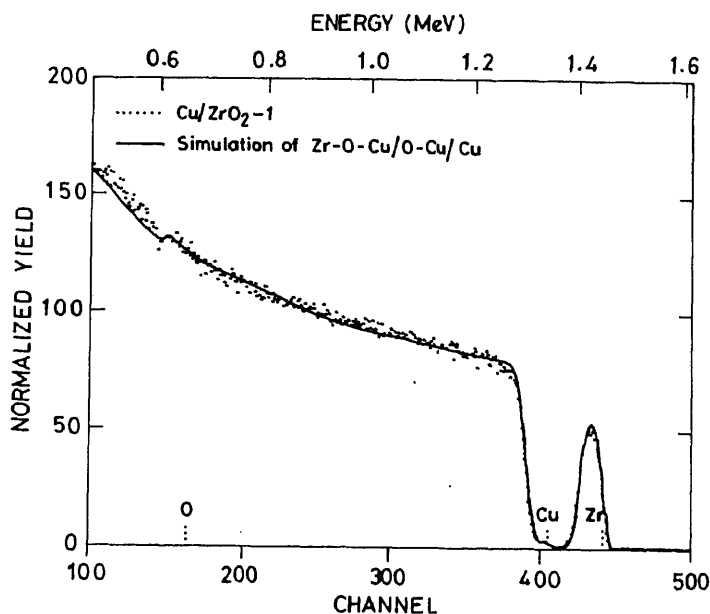


Figure 4. RBS spectra of zirconia films deposited at optimized conditions.

assisted deposited films of AlN , the compound formation is due to diffusion of nitrogen into the growing film and that it is accelerated due to ion bombardment. They also observed that it was a strong function of the ion to atom arrival ratio, which in the present case is determined by the oxygen backfill pressure, deposition rate and target power. Unlike in ion assisted deposition, however, these parameters cannot be independently controlled in magnetron sputtering. The exact dependence of compound formation of these factors independently is therefore difficult to determine.

Another factor of significance is the existence of a critical oxygen pressure above which the properties of the films seem to be optimal. The pressure of oxygen can, thus also be used to modulate the optical properties of oxide films deposited using reactive magnetron sputtering.

All further studies were carried out on films deposited at the critical oxygen pressure of 3×10^{-5} torr and a total pressure of 2×10^{-2} torr, a deposition rate of 32 nm/min corresponding to a target power of 450 W.

One of the main problems related to the growth of zirconia thin films is intrinsic optical inhomogeneity. Optical inhomogeneity can be defined as the variation of refractive index across the thickness of a film, as a result of process parameters, changes in microstructure or composition or a combination of these. A material is considered to show positive inhomogeneity with respect to thickness if the refractive index increases from the film-air interface to the substrate-film interface and negative inhomogeneity in the reverse case. This translates into higher reflectance than the bare substrate for the film, in the former case and lower in the latter case.

Figure 5 shows the spectral reflectance curves for the films deposited at the optimized conditions (stated above), in their as deposited state and then post deposition annealed to temperatures indicated in the figure. It can be seen that while as deposited films show positive inhomogeneity, presumably due to non stoichiometry in the films, the films annealed to 300°C show almost homogeneous behaviour. Further annealing to 500°C and 850°C results in negative inhomogeneity. This can be attributed to the grain growth resulting from annealing, which in turn results in increased grain size across the thickness of the film.

The behaviour of refractive index and extinction coefficient as a function of post deposition temperature shown in figures 6a and b respectively at three different wavelengths is illuminating. It is observed that up to a temperature of 300°C both the refractive index and extinction coefficient do not show very drastic changes as in the case of inhomogeneity. However beyond 300°C while the index drops, the extinction coefficient rises sharply and saturates beyond 500°C, both the optical constants show another step beyond 800°C. This signifies the fact that the optical constants are not stable to thermal annealing and show large changes in their values. Initially, however, they seem to be stable up to 300°C, as they approach

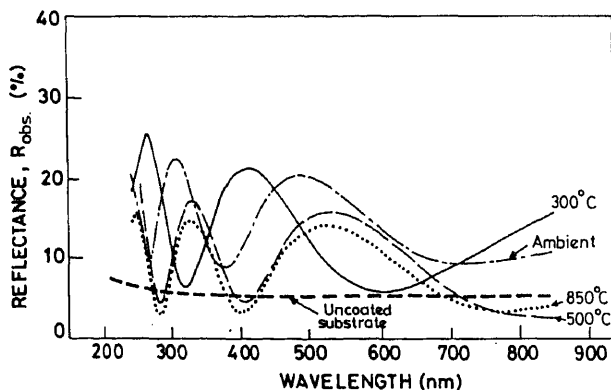


Figure 5. Spectral reflectance characteristics for as deposited and annealed zirconia films.

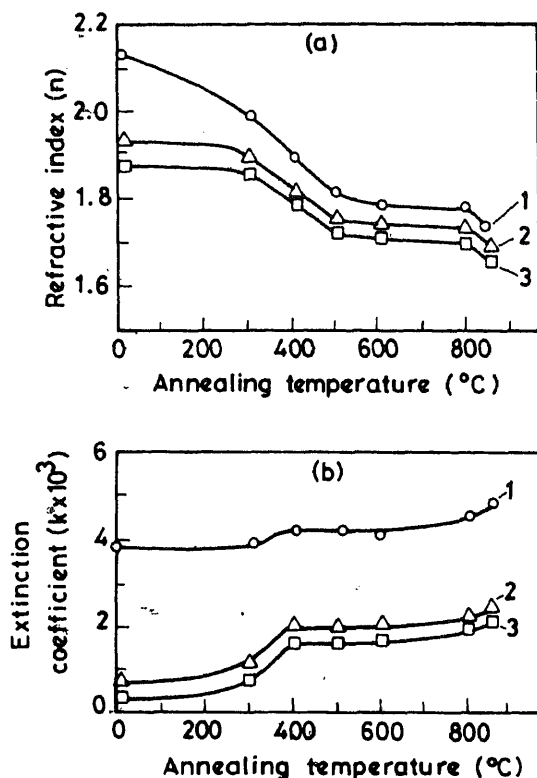


Figure 6. Optical constants as a function of post deposition annealing temperatures at (1) 350 nm, (2) 550 nm and (3) 850 nm.

zero inhomogeneity. Thus the inhomogeneity, the microstructure and the optical constants seem to, in conjunction, contribute to the instability of these films to thermal annealing.

The structural behaviour of these films is shown in figure 7, using X-ray diffraction. It was found that up to 400°C the films were completely amorphous and at this temperature they made a transition to a crystalline phase which was a mixture of tetragonal and monoclinic phase (figure 7a). The films were polycrystalline with small grain sizes, of the order of 12 nm (as estimated from the full width at half maximum of the peaks). At 600°C (figure 7b) the films were still polycrystalline with only a slight increase in grain size and finally at 900°C (figure 7c) they were almost single phase monoclinic, with a grain size of 24 nm. Two significant points that can be observed is that the films are mainly biphasic, i.e. they exhibit crystalline inhomogeneity in addition to optical inhomogeneity. Further the reduction in intensity of the tetragonal seems to be accompanied by an increase in grain size. This indicates a possible grain size dependent tetragonal to monoclinic phase transition. Such a transition has been observed earlier by Farabaugh *et al* (1987). It would thus appear that the instability to thermal annealing of zirconia with respect to its optical and structural properties is interrelated and that to exactly determine the cause for such behaviour would require further studies. Similar

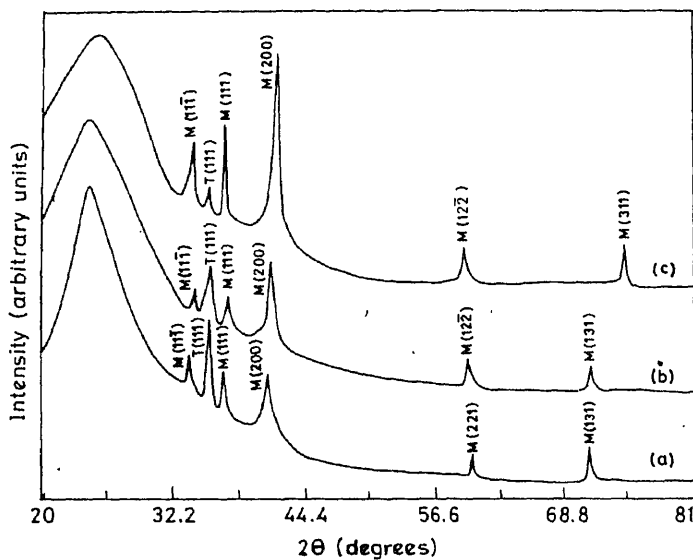


Figure 7. X-ray diffraction patterns for films annealed at a. 400°C, b. 600°C and c. 900°C.

observations have been made by Ghanashyam Krishna *et al* (1990) and Rujkorakarn and Sites (1986).

4. Summary

In summary, it has been demonstrated that zirconia films with reasonably high index and low optical absorption can be deposited at low temperatures by reactive DC magnetron sputtering. The composition of the films deposited under optimized conditions shows that the films are nearly stoichiometric. The refractive index, optical band gap and extinction coefficient are strong functions of the deposition parameters. The thermal stability of these films, however needs to be improved to enable larger applications of these films.

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The mechanical response of tetragonal zirconia polycrystal to conical indentation

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Abstract. Blocks of 3Y-TZP were indented with conical diamond indenters. Indentation caused tetragonal to monoclinic phase transformation in a subsurface. Of the cracks generated in the subsurface, radial and lateral cracks can be accounted for by a continuum model of the indented subsurface, built using a combination of the Boussinesq and blister stress fields. Additional ring, median and cone cracks were also observed. It is hypothesized that the latter are motivated by the reduction in blister strength or residual energy brought about by the material damage caused by the phase transformation. This damage reduces the load bearing capacity of the material progressively with increasing normal load.

Keywords. TZP; conical indentation.

1. Introduction

Metastable tetragonal zirconia-based ceramics have attracted attention in engineering because of their ability to undergo stress-induced transformation toughening. The effect of dilatational and shear stresses on transformation plasticity of these materials have been discussed by Chen and Reyes-Morel (1986). In this and other (Marshall and James 1986; Martinez-Fernandes *et al* 1991) studies indentation by a rigid indenter has often been used to induce transformation and to note the resulting mechanical response of the material.

The present paper is concerned with the elasto-plastic response of TZP (tetragonal zirconia polycrystal, 90% tetragonal phase) to the stresses introduced by indentation. The damage inflicted on this material which is prone to stress-induced phase transformation and plasticity at room temperature, is studied here by observing the changes in the load bearing capacity with normal load and initiation of crack modes, especially the additional modes believed to be initiated due to phase transformation. The usefulness of such a study lies in interpreting data obtained from impact erosion and abrasive wear.

Cook and Pharr (1990) and Yoffe (1982) studied the indentation fracture behaviour of soda lime glass and other ceramics by employing elasto-plastic continuum analysis. They predict the initiation of a crack type by observing the directionality of the tensile stress. As transformation causes 4% volume expansion and local damage, often in the form of transformation pits in the transformed volume, the stress field in this volume cannot be determined easily using continuum theories of elasticity and plasticity. It is for this reason that the present problem is addressed in two stages. The material is first idealized such that its response to indentation is purely elastic involving no phase transformation. An elastic stress field is used at this stage to identify the possible crack types which will be initiated given the

elastic constants of TZP. The cracks observed experimentally in addition to these types are then stated to be due to phase transformation. The possible reason for the generation of these additional cracks is discussed.

In comparing the competence of the three proposed (Chiang *et al* 1982; Yoffe 1982; Johnson 1985) stress fields in elasto-plastic indentation of copper, Ghosal and Biswas (1992) have recently found Yoffe's stress field to be the most competent one in predicting the surface strain distribution. Mukhopadhyay and Biswas (1991) and Cook and Pharr (1990) found Yoffe's stress field useful in describing mechanical response of brittle materials to indentation. In the present work Yoffe's stress field is used to describe the nature of stresses generated by indentation in the TZP subsurface.

2. The stress distribution

The elastic stress field proposed by Yoffe consists of two components: a Boussinesq field dependent on applied normal load and varying inversely with the square of the distance and a blister field originally due to Love (1920) determined by the extent of permanent deformation. The stresses due to the latter vary inversely with the cube of the distance. The stress components in polar (r, θ, ϕ) coordinates are,

$$\sigma_r = (L/2\pi r^3) [1 - 2\nu - 2(2 - \nu) \cos \theta] + 4(B/r^3)[(5 - \nu) \cos^2 \theta - (2 - \nu)], \quad (1a)$$

$$\sigma_\theta = (L/2\pi r^3) [(1 - 2\nu) \cos^2 \theta / 1 + \cos \theta] - 2(B/r^3) (1 - 2\nu) \cos^2 \theta, \quad (1b)$$

$$\sigma_\phi = L(1 - 2\nu)/2\pi r^2 [\cos \theta - (1/1 + \cos \theta)] + 2(B/r^3) (1 - 2\nu) (2 - 3 \cos^2 \theta), \quad (1c)$$

$$\tau_{r\theta} = (L(1 - 2\nu)/2\pi r^3) (\sin \theta \cos \theta / 1 + \cos \theta) + 4(B/r^3) (1 + \nu) \sin \theta \cos \theta, \quad (1d)$$

where L is the applied load, ν the Poisson's ratio, and B the blister field strength expressed in units of energy.

Cook and Pharr (1990) estimates the parameter B from volume considerations. The volume swept by any hemisphere of radius r measured from the point of indentation may be found by applying Hooke's law to the stress field given by (1):

$$\Delta v = 2\pi B (1 - 2\nu)/3G,$$

where G is the shear modulus.

Now the volume displaced by a conical indenter of included angle 2α is

$$\Delta v = \Pi h_r^3 \tan^3 \alpha / 3, \quad (2)$$

where h_r is the residual indentation depth.

Equating (1) and (2) gives

$$B = f [Eh_r^3 \tan^3 \alpha / 4 (1 - \nu) (1 - 2\nu)], \quad (3)$$

where E is the Young's modulus and f the densification factor. Cook and Pharr (1990) note that the densification factor for a commercially compacted and sintered ceramic is 1. With reference to (1), the parameter B is seen to be directly related to the residual stress ($L = 0$) and it has the units of energy. Lawn and Howes (1983) associated a permanent indent in elastic-plastic indentation with a residual energy analogous to that stored in a pre-compressed spring. On release of this residual energy the indenter depth is reduced to zero. If this concept is correct as is demonstrated by Lawn and Howes (1983), it is likely that the parameter B is directly associated with such a residual energy deposited in an indent.

3. Experimental

The test material is tetragonal zirconia polycrystals (TZP, 80% tetragonal phase) of density 6.05 g/cm^3 , Vicker's hardness 13 Gpa, Young's modulus 205 Gpa and Poisson's ratio 0.3. Cylindrical specimens of 5 mm dia and 5 mm length specimens were cut using a low speed diamond saw from a commercially obtained 5 mm dia TZP rods. The as cut surface of roughness $0.1 \mu\text{m}$ CLA was indented using diamond conical indenters of cone angle and 150° . The indentation was carried out in quasi static mode. The specimen was placed on a (5 kN maximum) load cell. A schematic of the indentation rig is given in figure 1. The displacement of the load cell due to 4 kN (maximum experimental load) compressive load is $\approx 4 \mu\text{m}$. Considering that this order of displacement is very small compared to the indentation depths of the order of $160 \mu\text{m}$ measured at this order of load, the reported penetration depth can be taken to be a reasonable representation of the true penetration depth. The load L was continuously measured during experiment as a function of the penetration depth h which was measured by an LVDT placed on a rigid platen

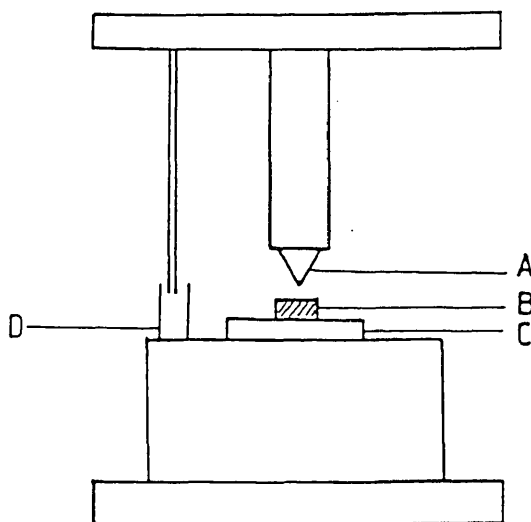


Figure 1. A schematic of the indentation set up (A, indenter; B, specimen; C, load cell; D, LVDT).

which also supported the load cell. The whole assembly was placed inside a precision subpress which was driven hydraulically in a universal testing machine. The surface zone and the diametral cross-section of the subsurface zone were examined by SEM and optical microscopy.

4. Results

4.1 Influence of transformation on load-penetration characteristics

Loubet (1986) gives the load-penetration relation in conical indentation of elasto-plastic material as

$$P = Kh^2, \quad (4)$$

where h is the depth of penetration and K a constant given by

$$K = [(1/\pi H \tan^2 \alpha)^{1/2} + \{2(1 - \nu^2)/\pi E \tan \alpha\}^{1/2}]^{-2}.$$

Table 1 gives the hardness of cubic, tetragonal and monoclinic phases of zirconia. The Young's modulus is structure insensitive. Figure 2 shows the theoretical

Table 1. Hardness and Young's modulus of zirconia.

Constituent	H (GPa)	E (GPa)	References
Cubic	15.5		Chen and Reyes-Morel (1986)
Tetragonal	13	205	Test material
Monoclinic	6.5		Chen and Reyes-Morel (1986)

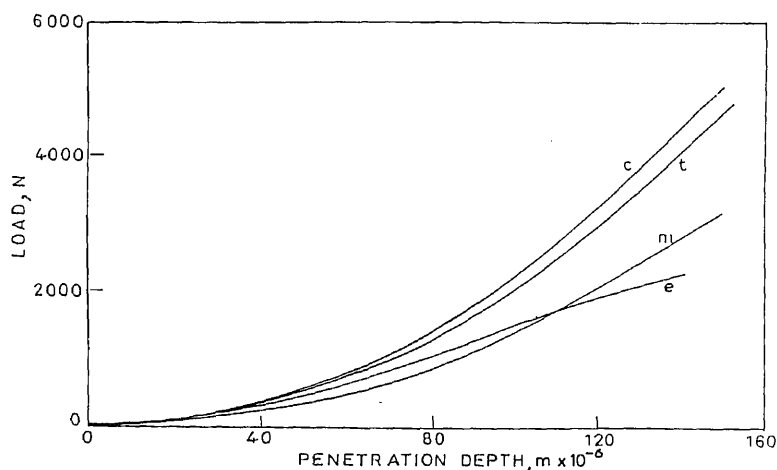


Figure 2. Load-penetration in indentation by a 150° diamond cone. Predicted characteristic for monophase zirconia (c, Cubic; t, tetragonal; m, monoclinic; e, experimental characteristics for tetragonal zirconia polycrystals).

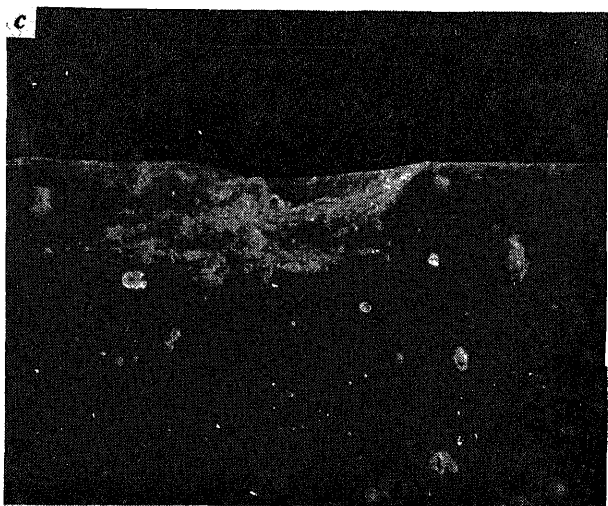


Figure 3a-c. For caption, see page 869.

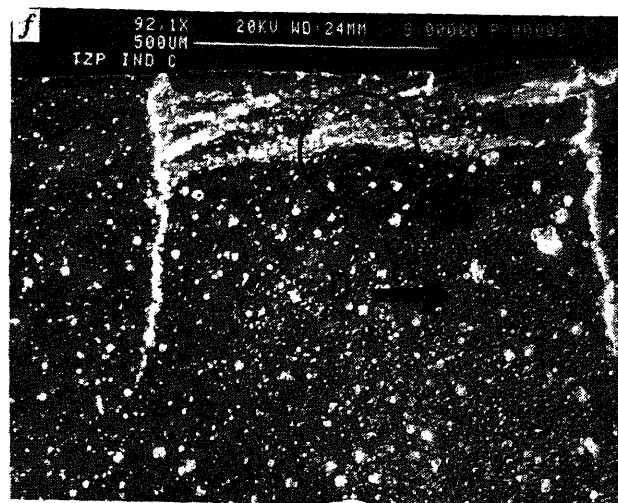
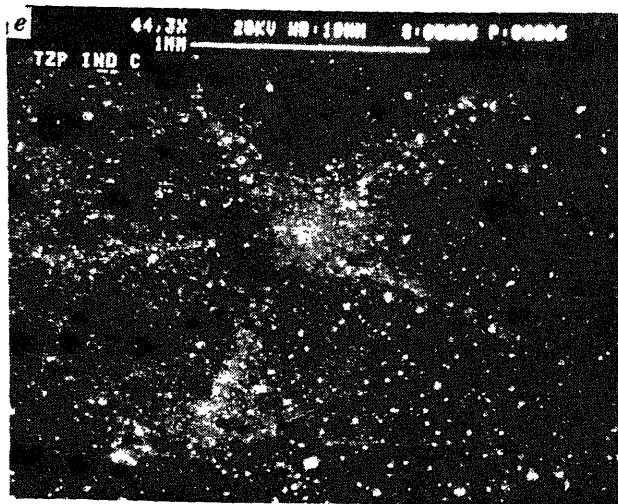
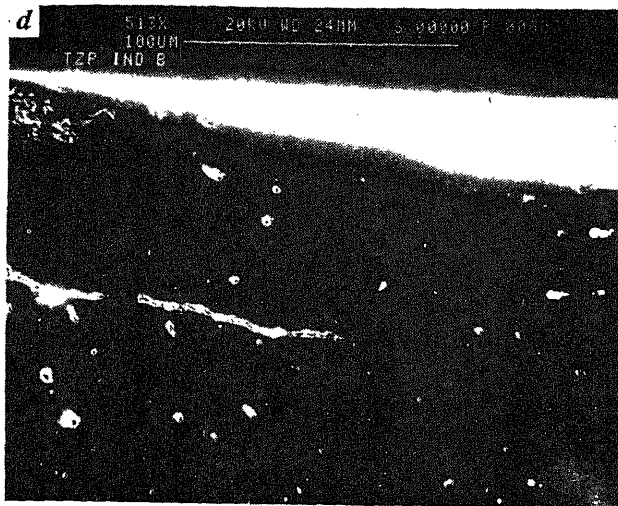


Figure 3d-f. For caption, see page 869.

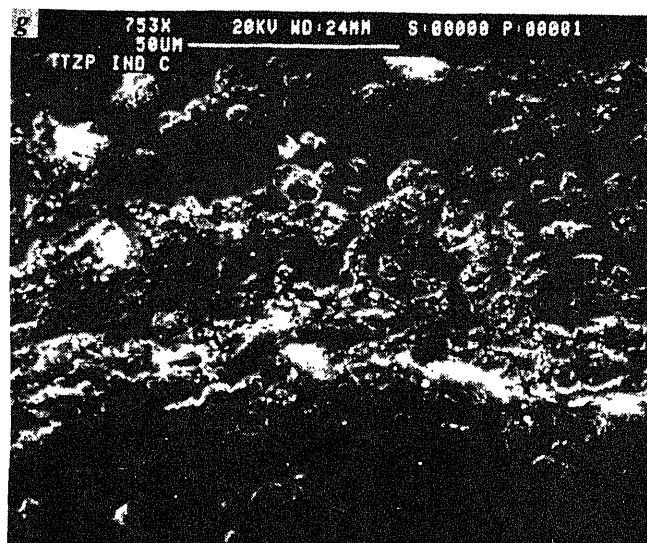


Figure 3. a-g. a. Surface SEM micrograph of 150° conical indentation loaded to 1900 N showing ring and radial cracks: (---) periphery of the indent; (B) ring crack, b. magnified view of the circled region of figure 3a showing radial (marked C) and ring (marked B) cracks, c. subsurface SEM micrograph of 150° conical indentation loaded to 1900 N, showing deformed zone, d. subsurface micrograph of 150° conical indentation loaded to 1900 N, showing lateral cracks, e. surface micrograph of 150° conical indentation loaded to 3750 N, showing radial cracks with heavily pitted zone, f. subsurface micrograph of 150° conical indentation loaded to 3750 N, showing median (marked D), cone and lateral cracks with heavily pitted zone and g. a magnified view of the circled region of f showing heavily pitted and disturbed region left in the wake of lateral crack.

load-penetration curves for all the three monophase materials estimated using (4).

Figure 2 shows that at loads below 1000 N the experimental load-penetration curve is in close agreement with that of the theoretical load-penetration curve of the tetragonal monophase material. At loads higher than 1000 N the experimental curve deviates significantly from the tetragonal curve with increasing load and tends towards the monoclinic. At higher loads (above 1900 N) the theoretical monoclinic curve overestimates the experimental results. This is indeed possible if there is a transformation of the original (85%) tetragonal phase during loading to a low load bearing monoclinic phase, and accumulation of contact mechanical damage.

4.2 Fracture behaviour

The fracture behaviour of TZP is studied here by indenting it with a 150° included angle cone loaded to a maximum load of 3750 N. The surface containing the indent and the cross-section of the indented block (containing a diametral section of the indent) are viewed in SEM to observe the cracks corresponding to the two indentation loads (figure 3). To study the fracture behaviour, the elastic stresses in the subsurface are computed using (1) and the nature of the three orthogonal stresses (σ_ϕ , σ_r , σ_θ)

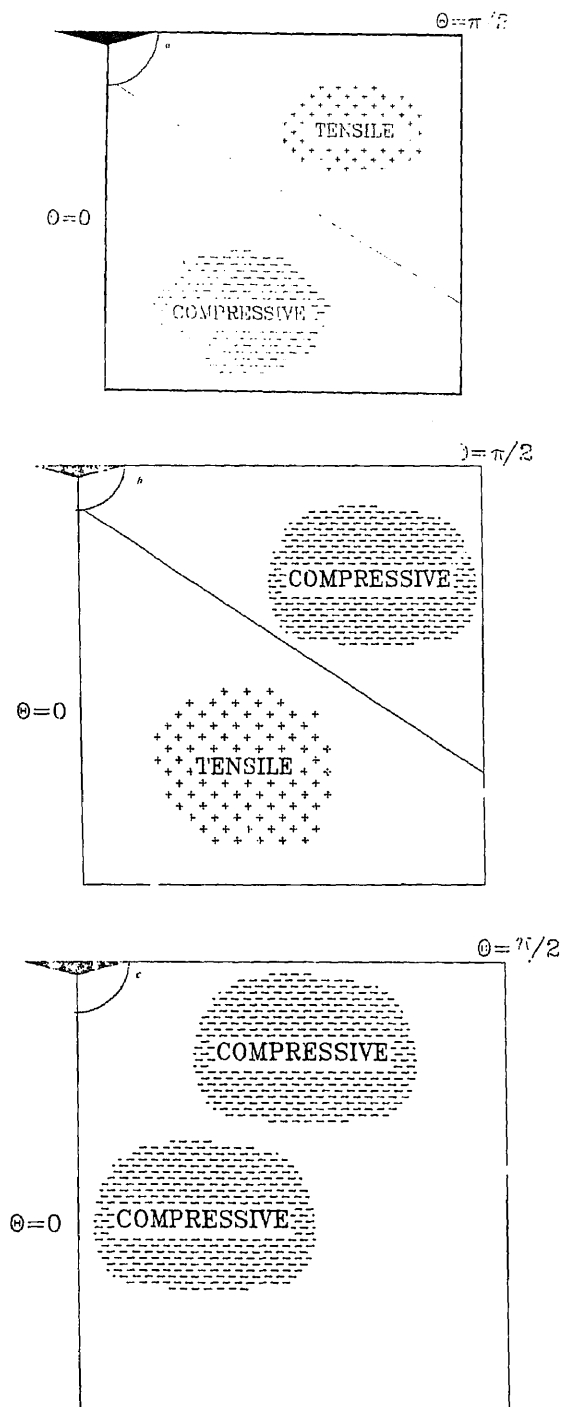


Figure 4. Indentation stress field as per (1). a. σ_θ , hoop stress; b. σ_r , radial stress; c. σ_θ , tangential stress.

is shown in figure 4. Considering that the stresses in the blister are highly compressive figure 4a indicates the possibility of a radial crack initiating at the edge of the contact where the tensile hoop (σ_ϕ) stress is maximum. Figure 4c indicates the possibility of lateral crack initiation (σ_r is tensile). Experimental observations, especially the fact that the radial crack is initiated at the contact edge (figure 3b), support the above predictions. It has to be noted that the nature of the subsurface stress field as shown in figure 4 do not change with the normal load. For the present material as the blister field is dominant over Boussinesq fields, (1) gives that the nature of σ_r and σ_ϕ do not also change on unloading ($L = 0$) but the stresses become more accentuated on unloading. Unloading thus cannot cause any new crack type to appear but it may help to propagate the already existing radial and lateral cracks or the radial and lateral cracks may become more numerous. Table 2 summarizes experimental observations and the theoretical predictions of crack initiation.

Figure 3 and table 2 show the presence of additional cracks; ring crack at low loads and ring, median and cone cracks at high loads, cracks which are not accounted for in the model behaviour of the idealized elastic material. These additional cracks may arise due to the different crack types interacting energetically. Cook and Pharr (1990) attributed the appearance of the secondary radial cracks in the indented anomalous soda lime glass to the release of residual energy caused by the nucleation and propagation of primary cone cracks.

Figures 3b–f show that radial and lateral cracks when they propagate leave in their wake heavily pitted and disturbed regions. Figure 3g shows a magnified view of such a region left in the wake of a lateral crack. Reece *et al* (1992) used Raman microprobe to identify such pitted regions as regions which have undergone phase transformation from tetragonal to monoclinic. They ascribe the pitting to the reduced bonding between adjacent grains because of microcracking produced during phase transformation. Such pitting is likely to reduce the residual energy (directly associated with B in §2) and open up the possibility of secondary crack types. Figure 5 shows the variation of stresses, computed using (1), with B . Figure 5a shows that if the material damage at the low load (1900 N) reduces the B values

Table 2. Indentation cracking in zirconia.

Cracks	Load 1 (1900 N)		Load 2 (3750 N)	
	Exp.	Theor.	Exp.	Theor.
Radial	Y (figure 3b)	Y (figure 4a)	Y (figure 3e)	Y (figure 4a)
Ring	Y (figure 3a)	N (figure 4b)	Y (figure 3f)	N (figure 4b)
Lateral	Y (figure 3d)	Y (figure 4b)	Y (figure 3f)	Y (figure 4b)
Median	N (figure 3c)	N (figure 4c)	Y (figure 3f)	N (figure 4c)
Conical	N (figure 3c)	N (figure 4b)	Y (figure 3f)	N (figure 4b)

Y, Yes; N, No.

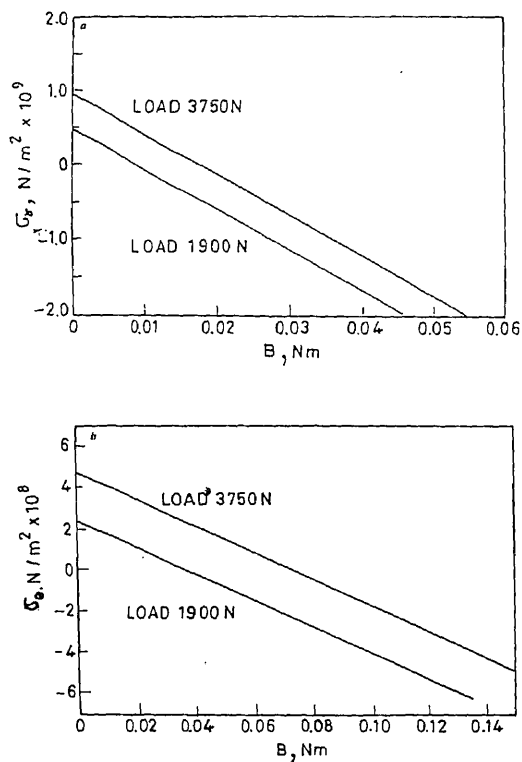


Figure 5. Variation of stresses with B . a. σ_r at $r = 500 \mu\text{m}$, $\theta = 90^\circ$ and b. σ_θ at $r = 500 \mu\text{m}$, $\theta = 0^\circ$.

from 0.134 Nm (calculated using (3)) to 0.01 Nm, the σ_r becomes tensile, creating the possibility of a ring crack initiation at low load. While less material damage ($B = 0.36$ to 0.05 Nm) is required (figure 5b) to initiate a median crack at this load (3750 N), the order of σ_θ ($\theta = 0^\circ$) may be too low (half that of the corresponding σ_r , at $B = 0$) for that to happen. It is considered that with an increase in normal load the extent of material damage due to phase transformation in the subsurface increases and the subsurface stresses become more and more tensile. At high load the ring crack at the surface may propagate into the subsurface to give rise to a cone crack. Figure 5b shows that σ_θ ($\theta = 0^\circ$) at this load becomes tensile at about 0.08 Nm and the level of the stress is also doubled (at $B = 0$) due to the load increment. Increment in load would thus tend to encourage the initiation of a median crack. With increasing load more crack types thus come into existence and the load bearing capacity becomes increasingly less than that of a purely monoclinic material at high loads, as seen in figure 2.

5. Conclusions

3Y-TZP blocks were indented by conical diamond indenters. The material underwent phase transformation from tetragonal to monoclinic leaving highly pitted and disturbed

region in the transformed subsurface. An attempt was made to separate the crack initiation due to a purely elastic response of the material from that due to phase transformation. A combination of near field stress regime due to a blister which account for the permanently deformed material and a far field regime due to the Boussinesq point force was used to describe the elastic stress field due to indentation. At low loads the radial, lateral and ring cracks and at high loads additional lateral, median and cone cracks were observed.

A purely elastic response of TZP to indentation can initiate radial and lateral cracks. The material damage caused by phase transformation can initiate a ring crack at low loads by lowering the residual energy. As the load is increased the damage becomes extensive paving the way for an extension of the ring crack to a cone crack and the initiation of a median crack.

This progressive weakening of the material caused by an increase in indentation load is considered to be responsible for the corresponding reduction in load bearing capacity.

Acknowledgement

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Studies on high temperature deformation behaviour of 3Y-TZP ceramics

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Abstract. The present work reports the results on the deformation behaviour of ZrO_2 -3 mol% Y_2O_3 (3Y-TZP) ceramics which were prepared by pressureless sintering at 1400°C. Dense, cylindrical samples were subjected to uniaxial compression tests under a constant stress of 15 MPa in the temperature range of 1200–1400°C. The ceramics exhibit considerable ductility, attaining over 60% true strain without any edge cracking. Microstructural changes due to interaction of grain boundary viscous phase with the ultrafine and equiaxed grains were analyzed by transmission electron microscopy. Results show the grain boundary sliding accompanied by a diffusion accommodation process as the predominant deformation mechanism in these ceramics.

Keywords. Yttria stabilized zirconia; superplasticity; microstructure; TEM.

1. Introduction

Y_2O_3 stabilized tetragonal ZrO_2 polycrystals (Y-TZP) form one important class of transformation toughened ceramics. These ZrO_2 based alloys are promising structural materials for various high performance applications because of their excellent mechanical properties such as strength and toughness. It has also been observed that these ceramics fulfil many of the microstructural prerequisites that have been established for superplasticity in metals and alloys. Subjecting ceramics to deformation forming is thus an important recent advancement in fabrication technology (Panda *et al* 1988; Chen and Xue 1990). Dense Y-TZP ceramics obtained on sintering at moderate temperatures ($\sim 1400^\circ\text{C}$) exhibit a homogeneous single phase (tetragonal- ZrO_2), microstructure consisting of ultrafine ($<1.0\ \mu\text{m}$) and equiaxed grains. The impurities introduced during processing often contribute to the grain boundary liquid phase by the formation of low temperature eutectic melts (Lang *et al* 1986). Extensive studies have been carried out in tailoring a microstructure which is stable against coarsening during deformation at elevated temperatures. A suitable modification of grain boundary chemistry by incorporating some system specific dopants (MnO , CoO) and by providing a composite configuration with other oxides (e.g. Al_2O_3) is usually followed in these systems (Kimura *et al* 1988; Wakai 1989; French *et al* 1990; Upadhyaya *et al* 1993a, b).

The mechanism of superplasticity in ceramics is not fully understood. It is generally explained in terms of models based on the grain boundary sliding or diffusional flow mechanisms (Wang and Raj 1984; Wakai *et al* 1989). The constitutive equation for deformation in polycrystalline samples at elevated temperature has the form:

$$\dot{\epsilon} = A (\sigma^n / d^p) \exp (-Q/RT), \quad (1)$$

where A is the deformation mechanism dependent function, d the mean grain size, p the grain size exponent and n the stress exponent (reciprocal of strain rate sensitivity). The other symbols in above equation have the usual significance.

For Y-TZP ceramics, a large discrepancy appears in the value of n reported by different authors (from 1.1 to 3.5) (Wakai 1989). The difference in behaviour and a predominantly non-Newtonian flow ($n > 1$) mechanism is likely to be dependent on the concentration and nature of the grain boundary glassy phase. Present work tries to analyze the interaction mechanism of the two microstructural parameters, viz. the rigid grains and soft boundary phase (glassy) in 3Y-TZP ceramics at high temperatures, under compressive loading conditions using TEM as a tool.

2. Experimental

The wet chemistry, co-precipitation route was employed to prepare fine powder of ZrO_2 -3 mol% Y_2O_3 . The starting material was 3N purity salts of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. Mixed solutions (0.5 M) were added drop wise into a vigorously stirred liquor ammonia bath which produced a white, gelatinous substance precipitated. These hydroxide gels were filtered, washed, dehydrated with ethanol and dried in air oven at 110°C . The dried mass was pulverized, calcined at 600°C for 3 h and ball milled for 8 h using Y-TZP grinding medium.

Cold compacted (84 MPa) samples on sintering at 1400°C for 2 h attained nearly full (98% TD) densification. Test samples (10 mm height $\times$ 10 mm diameter) were prepared with their parallel faces fine polished and coated with BN powder. The uniaxial compression experiments were carried out between 1200 and 1400°C in vacuum (10^{-3} Pa) at a constant load of 15 MPa. Tests were terminated at a true strain of about -0.6 in order to avoid nonuniform stresses and friction conditions. For microstructural investigations the deformed samples were diamond sawed to about $150\ \mu\text{m}$ sections. The 3 mm diameter discs were subsequently prepared by ultrasonic cutter and further mechanically thinned using disc grinder followed by dimple grinding using diamond paste. The final thinning to electron transparency was carried out in an argon ion mill operating at 4 kV. Carbon was deposited on the foils to prevent static charge accumulation during observation. A JEOL 2000 FX microscope was used for studying the microstructure.

3. Results and discussion

3.1 Undeformed 3Y-TZP ceramics

Microstructural features of the reference material are as shown by the typical micrograph in figure 1. It essentially shows a very fine grain structure ($\sim 250\ \text{nm}$) having a narrow size distribution. The as-sintered samples showed a dense structure, such that almost no porosity is found in both inter- and transgranular regions. The rounded shape of the grains is characteristic of the milled Y-TZP powders which have undergone densification by liquid phase sintering mode (Lang *et al* 1986; Lin *et al* 1990). The amorphous phase traps impurities and mainly segregates at the grain trijunction and also forming an apparently continuous intergranular thin film.

Presence of glassy phase is beneficial in relieving the residual stresses developed



Figure 1. Transmission electron micrograph of undeformed 3Y-TZP showing the rounded grains and glassy grain boundary phase.

during cooling due to anisotropic thermal contraction of t -ZrO₂ grains (Lin *et al* 1990). In the present material, the grains were thus free from tweed like structure due to strain field contrast found in high purity Y-TZP ceramics having straight boundaries with sharp apexes (Amana *et al* 1992). The grains rather exhibited a distribution of three twin related variants of t -ZrO₂. The frequency of occurrence of twins was very large with most of the twins revealing the presence of more than one variant in each grain with the different variants sometimes lying in a triangular arrangement.

Another significant observation was with respect to the occasional presence (in about 5% of the specimen area scanned) of the large ($> 1\mu\text{m}$) grains surrounded by an ensemble of significantly smaller size grains (figure 2). This anomalous growth of solute rich c -ZrO₂ grains is generally observed in Y-TZP on high temperature annealing (1500°C). Development of such microduplex structure due to equilibrium partitioning of yttria was found to be very effective in maintaining the fine grain size of Y-TZP ceramics (Lang *et al* 1985; Lang 1986). The large grains of the c -ZrO₂ were irregularly shaped unlike the smaller grains of t -ZrO₂ which were mostly spherical. Twin like features could be seen in some of the c -ZrO₂ grains.

3.2 Microstructural evolution after deformation

Dense 3Y-TZP samples in the shape of right cylinders were compression-tested

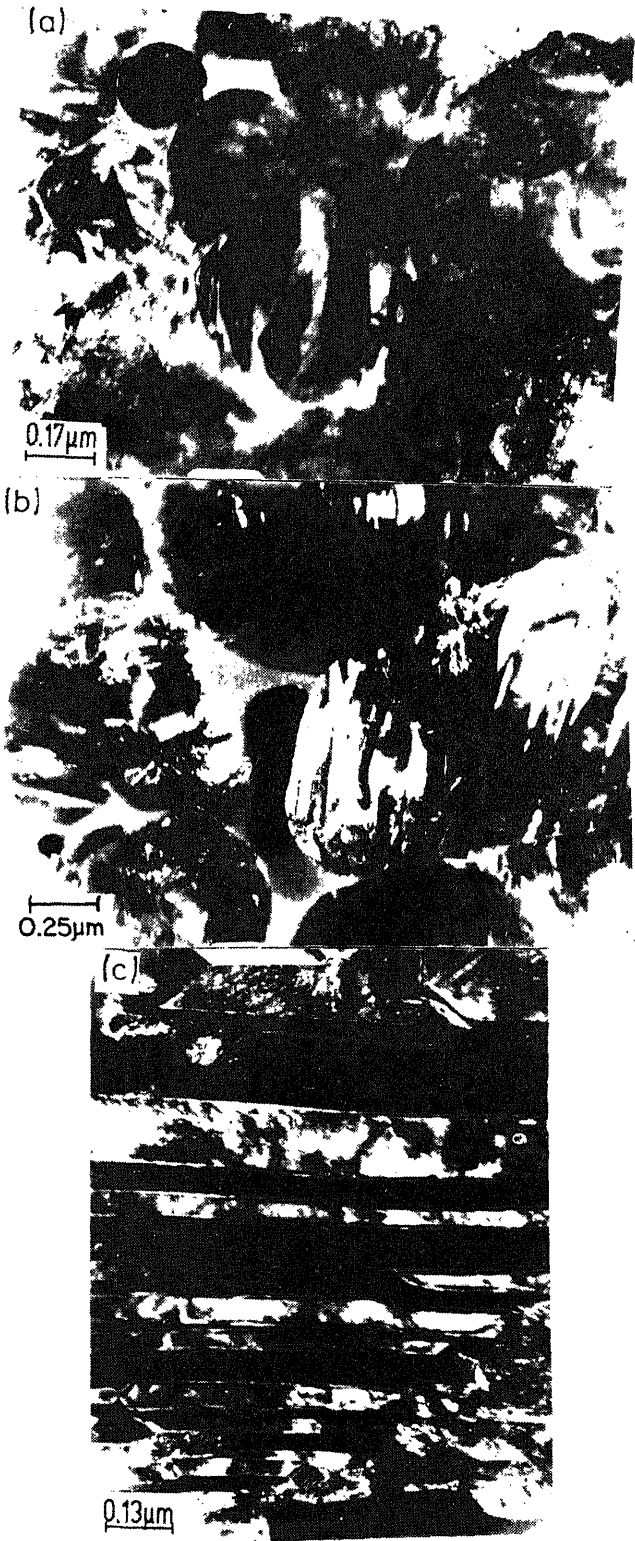
uniaxially at 1200–1400°C which is the thermodynamic stability range of tetragonal phase of ZrO_2 . The absence of transformation toughening in conjunction with the favourable microstructural parameters viz. ultrafine grain size and residual grain boundary viscous phase imparts appreciable plastic deformation before failure. The change in microstructure is as shown in figure 3(a–c) for the sample strained to 60% at 1400°C. It is observed that some amount of coarsening of grains takes place without affecting their isometric shape. The glassy phase is relocated (squeezed) in the form of thin intergranular film. It was possible to see grain boundary trijunctions having very little or no amorphous phase in between.

About the high temperature plastic deformation of bulk ZrO_2 alloy single crystals, considerable work has been done over the years. It is mostly the work of Heuer and coworkers (Dominguez-Rodriguez *et al* 1986; Cheong *et al* 1989, 1991; Fries *et al* 1989; Heuer *et al* 1989) which establishes that in Y-CSZ the deformation behaviour is very sensitive to crystal orientation together with other parameters, e.g. solute concentration, temperature and strain rate. Significant solid solution strengthening is observed over the range of compositions studied (9.4–21 mol% Y_2O_3). The yield and flow stress increase with increasing Y_2O_3 content. Similarly,



Figure 2. Bright field micrograph showing an occasional bimodal grain size distribution containing coarse $t\text{-ZrO}_2$ grain surrounded by a much finer $t\text{-ZrO}_2$ grain cluster.

Figure 3. Microstructural changes after plastic deformation of 3Y-TZP ($\epsilon = 60\%$, $T = 1400^\circ\text{C}$, $\sigma = 15\text{ MPa}$). **a.** Grains are coarsened but the isometric shape is retained, **b.** considerable squeezing of the grain boundary liquid into the residual pores and **c.** stress induced reorientation of ferroelastic domains in $t\text{-ZrO}_2$. Two sets of twin variants grow at the expense of third set to facilitate the stress accommodation.



in two-phase Y-PSZ single crystals the phenomenon of precipitation hardening is encountered. In these experiments the stresses employed are generally large (> 200 MPa) and alloy crystals exhibit predominantly a shear band deformation mode accompanied by excessive dislocation activity. Lankford *et al* (1988) supplemented these results by introducing the contributions from transformation plasticity and ferroelastic domain switching.

In the case of polycrystalline ZrO_2 based ceramics the situation is very complex due to grain boundary lubrication by an ubiquitous amorphous phase, for sliding mode to dominate. This permits only a phenomenological explanation by attributing it as the constituent responsible for the viscous-like flow during compression. Maintaining equiaxed grain shape even after extensive deformation is an important aspect which generally suggests a grain intercalation mechanism operating as those visualized in superplastic deformation conditions. An elongation of the grains in the direction perpendicular to the loading axis is predicted if diffusional creep prevails which is contrary to present observations. TEM also revealed that grains were nearly free of dislocations indicating a somewhat minor contribution of dislocation motion in the creep of Y-TZP, in the temperature and stress regimes employed in this work. Though the extent of deformation of the *t*- ZrO_2 grains was extremely small, the boundaries between the *t*- ZrO_2 and *c*- ZrO_2 grains showed considerable amount of waviness in some regions.

The grain boundary amorphous phase has a dual role in influencing the deformation behaviour of Y-TZP. It invariably leads to a strain enhanced dynamic grain growth because of high homologous temperature employed ($\sim 0.5 T_m$). This suggests that grain boundary sliding is accommodated by interface-reaction controlled diffusional creep in the presence of glassy aluminosilicate phase. The model of Pharr and Ashby (1983) describes the liquid enhanced creep on the basis of repetitive cycles of plasticity and dissolution. The macroscopic yielding of 3Y-TZP thus can be rationalized in terms of micrograin superplasticity which is due to the superposition of various mechanisms viz. grain boundary sliding, grain rotation, diffusional accommodation and viscous flow. In addition to this the possible role of important subgrain features of *t*- ZrO_2 , i.e. the ferroelastic twin rotation also needs to be evaluated. The domain switching is an intrinsic, thermally activated process involving migration of the interfaces separating the domains. This migration process generates a shear distortion in the fluorite lattice.

TEM is a useful technique for analyzing the change in twinning mode after deformation. Unlike the *t*- ZrO_2 grains of the undeformed control sample the grains of deformed specimens showed generally a single twin variant (figure 3c). This fact could be ascertained from the bright and dark field micrographs and corresponding selected area diffraction patterns. Presence of single twin variant was indicative of the occurrence of domain switching. This twin reversal is the unique stress accommodation parameter for 3Y-TZP ceramics and can contribute significantly towards deformation (Lankford *et al* 1988).

The foregoing discussions have pointed to the role of multiple parameters involved in the deformation processing of 3Y-TZP ceramics. From the mechanistic standpoint it can be understood to be completed essentially in three steps. In the initial stage, a lubricated flow begins due to liquid film migration and partial dewetting of the grain boundaries. The flow is sustained in the intermediate stage by solution-precipitation creep. A redistribution of liquid into the residual pores and other

lower energy sites, softens the stress concentration at the grain interfaces. In the final stage the solid-solid contacts are established between the grains and the above mentioned twin reversal process is activated. The different values of strain rate sensitivity exponent measured by different authors for their materials can be attributed to the difference in critical balance obtained between various stress relieving processes.

4. Summary

The present work deals with the superplastic deformation of 3Y-TZP ceramics during compressive creep testing up to true strain near 60% and the resultant microstructural development of the material. TEM results suggest a three-step process sequence basically comprising the redistribution of the grain boundary amorphous phase, the concurrent grain growth due to deformation enhanced diffusion and a stress accommodation due to subgrain ferroelastic domain switching of *t*-ZrO₂. The grain boundary amorphous phase plays a dominant role in controlling the flow properties of 3Y-TZP. The difference in its chemistry thus explains the discrepancy in the reported value of the deformation parameters.

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Microdeformations in ferroelectrics

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Abstract. Ferroelectrics undergo one or more crystallographic phase transitions, which involve lattice distortions. The direction of spontaneous polarization in ferroelectrics can be reoriented by an applied electric field (or mechanical stress). There is a spontaneous strain accompanying spontaneous polarization. Phase transitions and domain reorientations thus result in microdeformations. Many devices such as actuators and transducers are based on this behaviour. The origin of microdeformations in ferroelectrics and their consequences are discussed here.

Keywords. Microdeformations; ferroelectrics.

1. Introduction

It was a century ago that the first dielectric anomaly was reported, 75 years since the discovery of the first ferroelectric, namely, Rochelle Salt, 60 years since ferroelectricity was observed in hydrogen bonded potassium dihydrogen phosphate, KH_2PO_4 , and a half century since ferroelectricity was revealed in a stable oxide, namely barium titanate, BaTiO_3 .

The last-named family characterized by corner linking of oxygen octahedra has dominated the research and development efforts in the ferroelectric field in the last half century, because of the large number of compounds in this family, their stability and the wide range of dielectric, piezoelectric, electrostrictive and electrooptical properties exhibited by them. Oxide ferroelectrics are the subject of the present paper.

On cooling from elevated temperatures, these compounds transform from the paraelectric state to ferroelectric or antiferroelectric state at a transition temperature, called Curie temperature, T_c . Some materials undergo additional phase changes at lower temperatures. Similarly, crystal symmetry may be altered by the application of electric field or mechanical stress or by compositional changes. Such structural transformations involve lattice distortions, resulting in microdeformations. The magnitude of such deformations can be modified by solid solution formation, as in the lead zirconate titanate, PZT, system. Other factors affecting microdeformations in ferroelectrics need examination.

By definition of a ferroelectric, the direction of its spontaneous polarization can be altered by an applied electric field. Such a process results in microdeformations, due to the fact that the polar axis is longer than other equivalent crystallographic directions. Domain reorientations result on application of uniaxial mechanical stress also. The magnitude of these microdeformations obviously depend upon the axial ratios and the extent of domain reorientations, and can lead to microcracking in some extreme cases. This results in a degradation of desirable dielectric and piezoelectric properties. For example, under some conditions, ferroelectric ceramics exhibit ageing phenomenon and electric fatigue, limiting their usefulness. Understanding the domain processes and the factors influencing them can be utilized to inhibit the onset of

ageing and electric fatigue. These issues have assumed importance for demanding applications such as actuators and memory devices (e.g. DRAMs) which involve cyclic loading and unloading (electrical or mechanical) over long periods and are examined here.

2. Phase transitions

The most studied ferroelectrics are barium titanate and related oxygen octahedra compounds. On cooling, they undergo one or more crystallographic phase transitions starting with a paraelectric to lower-symmetry ferroelectric state. These involve lattice parameter changes and lattice distortions, which may be small as in barium titanate (Kay and Vousden 1949) (figure 1a) or large and catastrophic as in lead titanate (Shirane and Hoshino 1951) (figure 1b). These distortions are studied largely by diffraction methods (X-ray and neutron). The dimensional changes of a ceramic BaTiO_3 (Shirane and Takade 1952) and PbTiO_3 (Shirane and Hoshino 1951), measured by a dilatometer, are shown in figure 2. The magnitude of ionic displacements and lattice distortions accompanying these PE-FE transitions are illustrated in figure 3 for BaTiO_3 (Jona and Shirane 1962) and compared with those in PbTiO_3 (Shirane *et al* 1956) in table 1.

The lattice parameter changes of simple perovskites (e.g. BaTiO_3 and PbTiO_3) may be compared with those of other oxygen octahedra ferroelectrics such as PbNb_2O_6

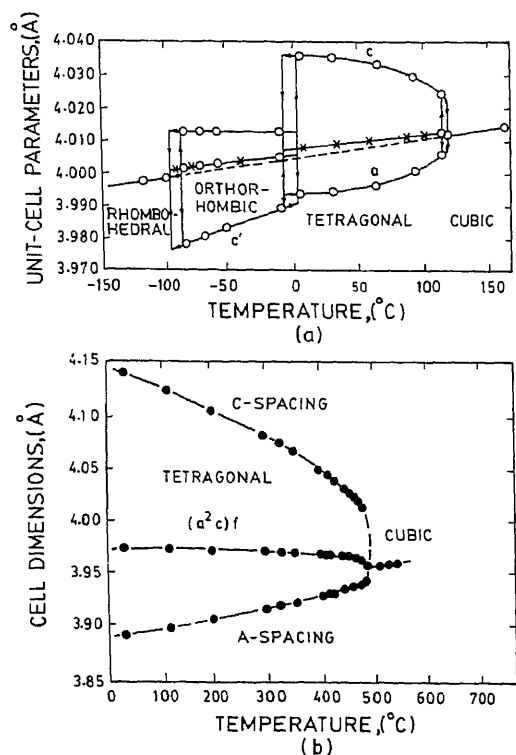


Figure 1. Temperature dependence of lattice parameters and lattice distortions of (a) BaTiO_3 and (b) PbTiO_3 .

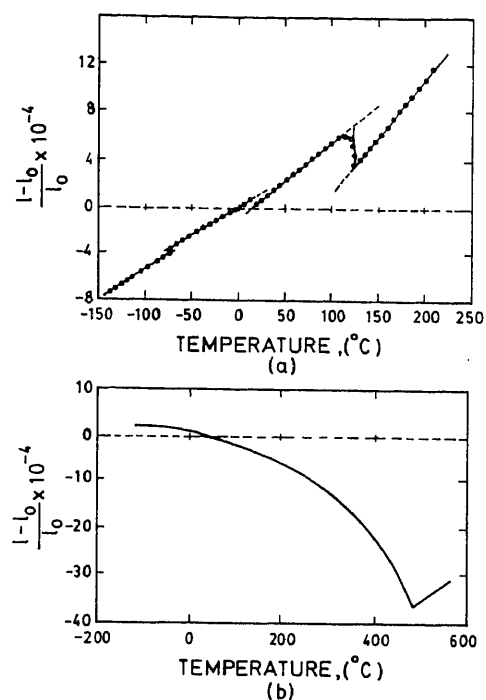


Figure 2. Fractional length change ($\Delta l/l$) of ceramic (a) BaTiO₃ and (b) PbTiO₃.

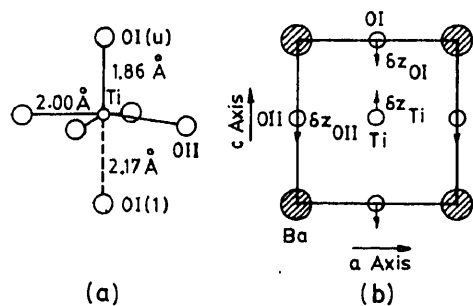


Figure 3. Ionic displacements in tetragonal (a) BaTiO₃ and (b) PbTiO₃ relative to cubic phase.

Table 1. Ionic displacements (in Å) in BaTiO₃ and PbTiO₃.

	BaTiO ₃	PbTiO ₃
δz_{Pb} or δz_{Ba}	0	0
δz_{Ti}	0.014	0.17
δz_{O1}	-0.023	0.47
δz_{O11}	-0.014	0.47

with a tungsten bronze structure (Subbarao 1960b) (figure 4a) and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with an Aurivillius-type layer structure (Subbarao 1961) (figure 4b). The lattice distortion at room temperature and the Curie temperature of these four compounds are listed in table 2. From these data, it is apparent that the microdeformation experienced due to lattice distortion at the phase transformation and due to anisotropic thermal contraction on further cooling to room temperature is much smaller in BaTiO_3 , PbNb_2O_6 and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ compared to PbTiO_3 , which, in fact, disintegrates on cooling through the transition. This, however, has been overcome by producing PbTiO_3 ceramics with a fine grain size, accomplished by the addition of about 2% Nb or Ta (Subbarao 1960a). It is interesting to note that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (and other members of this family) have exceptionally low lattice distortion (Subbarao 1962a) in spite of their high Curie temperatures (Subbarao 1962b) (even in comparison to BaTiO_3). The length changes experienced by ceramic specimens of PbNb_2O_6 (Subbarao 1960b) and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (Subbarao 1961) (figures 5a, b) relative to those of BaTiO_3 and PbTiO_3 (figures 2a, b) corroborate the behaviour of lattice parameter changes. These factors should have important implications for their electric fatigue behaviour on cyclic loading and unloading.

3. Domain reorientations

When an electric field is applied to a ferroelectric, the polar axis tends to align in the field direction. Since the polar axis is longer than equivalent crystallographic axes, the

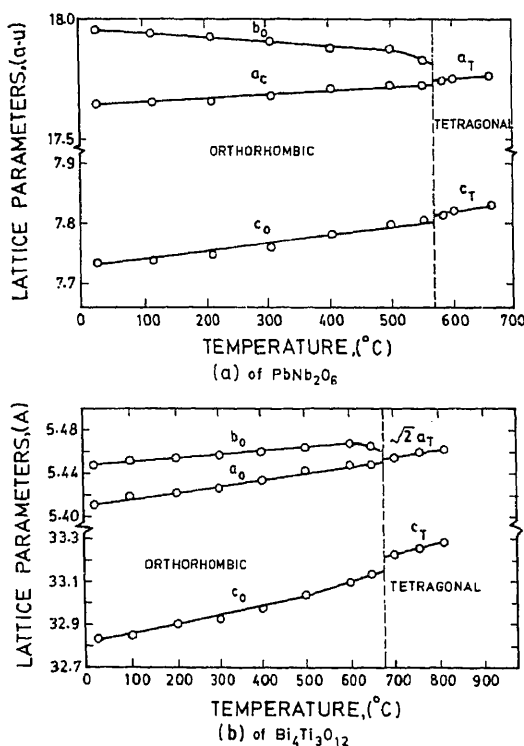


Figure 4. Lattice parameters vs temperature of (a) PbNb_2O_6 and (b) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

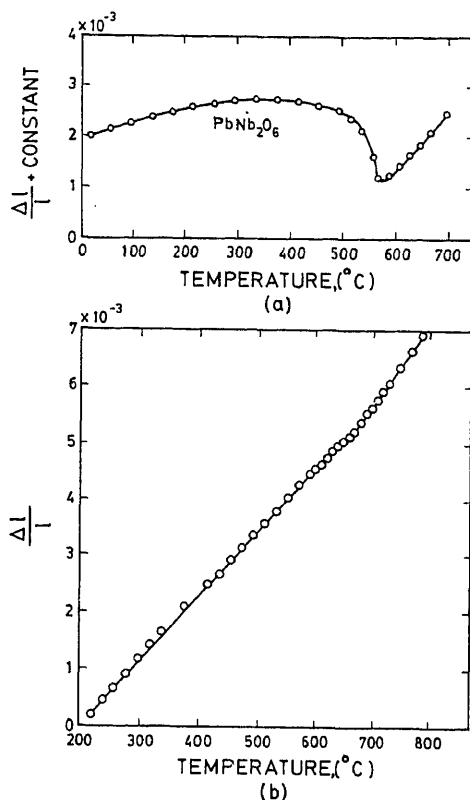


Figure 5. Fractional length change ($\Delta l/l$) of ceramic (a) PbNb_2O_6 and (b) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

Table 2. Lattice distortion at room temperature and Curie temperature (T_c).

Compound	Lattice distortion		T_c ($^{\circ}\text{C}$)
	b/a	c/a	
BaTiO_3		1.01	120
PbTiO_3		1.06	490
PbNb_2O_6	1.016		560
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	1.007		675

process of polar or domain reorientations result in dimensional changes. The magnitude of such changes depend upon the ratio of relevant lattice parameters (e.g. c/a in the case of tetragonal symmetry as in BaTiO_3 and PbTiO_3 and b/a in the case of PbNb_2O_6 and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$) (table 2) and the extent of domain reorientations. The magnitude of the applied electric field as well as hindrances to domain wall motions particularly in the case of ferroelectric ceramics determine the extent of domain reorientations.

A ferroelectric ceramic which has a random orientation of polar directions to start with undergoes domain reorientations to bring about alignment of polar axis into the

field direction when it is subjected to a d.c. electric field in a process called 'poling'. On removal of the electric field, some of the domains (imparting strain such as the 90° domains in tetragonal BaTiO₃ and lead zirconate titanate, PZT) revert to their original directions (Subbarao *et al* 1957), leaving some degree of preferred orientation of the polar axis in the field direction. If the domain reorientation results in strain beyond the strength of the material, the sample suffers microcracking which leads to deterioration of its electrical and piezoelectric properties. Recently, acoustic emission techniques were employed to follow dimensional changes accompanying domain reorientations during poling of PZT ceramics (figure 6a) including the onset of microcracking (figure 6b) when the magnitude or duration of electric field applications is large (Subbarao *et al* 1993). The deterioration of electrical properties as microcracking proceeds is shown in table 3.

Similarly, acoustic emission has been used to discriminate between domain switching and microcracking of lead lanthanum zirconate titanate (PLZT) ceramics during the application of an a.c. electric field for over 10⁸ cycles (Jiang *et al* 1994).

While the above discussion emphasized the dimensional changes accompanying domain reorientations in ceramics, similar phenomena occurs in ferroelectric single crystals as well. For example, Prasad and Subbarao (1972) applied an uniaxial stress to a single crystal of KNbO₃ and measured the dimensional changes in the stress direction and in the two directions perpendicular to it. An interesting relationship

$$\Delta x/x = -\Delta y/y \text{ and } \Delta z/z = 0,$$

was established and this was attributed to the reorientation of the 60° domains in the orthorhombic phase of KNbO₃ at room temperature. These changes were fully reversible. The duration of the application of electrical or mechanical stress on the dimensional changes has also been studied in the case of BaTiO₃ (Subbarao *et al* 1957; Prasad and Subbarao 1973).

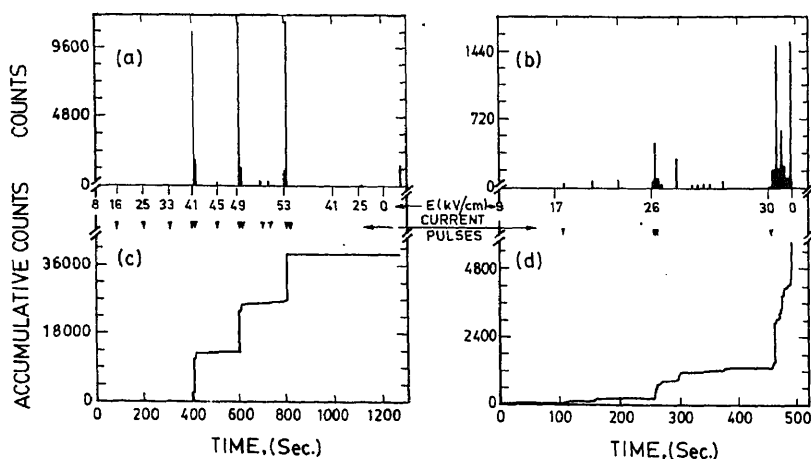


Figure 6. Acoustic emission count rate (a, c) and total AE counts (b, d) as a PZT sample was poled to successively higher fields before (a, b) and after the onset (c, d) of microcracking.

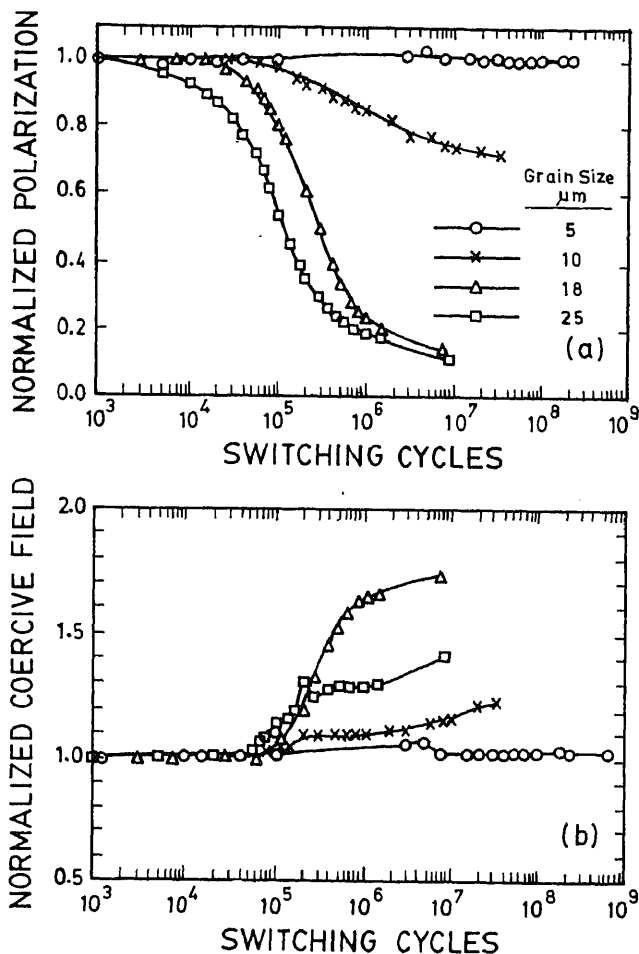


Figure 7. Normalized remanent polarization and coercive field as a function of switching cycles of hot pressed PLZT 7/68/32 ceramics with different grain sizes.

Table 3. Domain reorientations, microcracking and electrical properties of poled PZT.

Extent of poling and microcracking	d_{33} (10^{-12} C/N)	Q_M
Poled but no onset of microcracking	333	89
Poled till microcracking barely starts	350	65
Poled till microcracking starts	200	49
Poled till extensive microcracking has occurred	119	

4. Consequences of microdeformations

Microdeformations are a fact of life in ferroelectrics, as phase transitions and domain reorientations which take place in response to externally applied stimuli (temperature, pressure, electric field a.c. as well as d.c. and mechanical stress) inherently involve

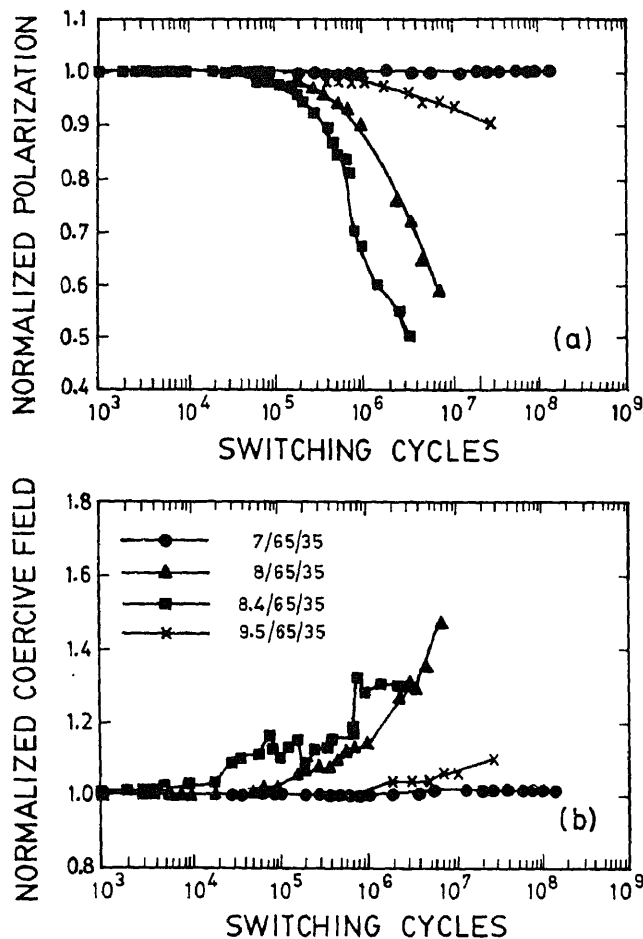


Figure 8. Normalized remanent polarization and coercive field as a function of switching cycles for hot pressed PLZT ceramics with compositions $x/65/35$.

dimensional changes. Spontaneous strain accompanies spontaneous polarization in ferroelectrics.

Microdeformations indeed form the basis for many applications of ferroelectrics in piezoelectric and electrostrictive devices such as transducers and actuators. Monitoring the microdeformations during poling of piezoelectric ceramics is worthwhile in order to arrest the poling process before the onset of the microcracking of the ceramic.

For reliable long-term performance of actuators and memory devices (e.g. DRAMs) which are subjected to cyclic mechanical or electrical stress, it is necessary to identify the underlying factors which affect the domain reorientation mechanisms—both intrinsic and extrinsic. An example of an intrinsic factor is the magnitude of the lattice distortion, with a preference for a smaller value to achieve long term stability. Thus, PZT is preferred to lead titanate for transducers. Bismuth layer compounds should be good candidates for DRAMs.

Extrinsic factors which affect domain reorientations are many. As an illustration, one may cite grain size of a ceramic. The case of fine grained lead titanate is already

mentioned (Subbarao 1960a). The PLZT ceramics suffered electric fatigue at 10^4 to 10^5 switching cycles when the grain size of the hot pressed ceramic is $10\text{ }\mu\text{m}$ or more whereas no decay in electrical behaviour (polarization and coercive field) was detected even beyond 10^8 switching cycles, if the grain size is $5\text{ }\mu\text{m}$ or less (Jiang *et al* 1994c) (figure 7).

It is well known that cubic (paraelectric), tetragonal and rhombohedral (ferroelectric) and orthorhombic (antiferroelectric) phases can exist at room temperature in the PLZT phase diagram (Haertling 1987). Compositions near the phase boundaries can undergo phase transformations under the influence of temperature or electric field. A number of compositions near the phase boundaries in this system were studied for their electric fatigue behaviour. It is clearly established that materials with rhombohedral symmetry exhibit little or no electric fatigue, compared to those with tetragonal or orthorhombic symmetry (with the degree of fatigue increasing with the lattice distortion c/a or b/a) (Jiang *et al* 1994b). The correlation between electric fatigue and crystal symmetry was first established by selecting compositions which possess different crystal structures at room temperature (figure 8) and was later confirmed by transforming the symmetry of a given composition by changing temperature or by applying electric field. In all these cases, the rhombohedral phase with its small shear distortion exhibited the least electric fatigue.

5. Conclusions

Ferroelectrics which undergo crystal structure transformations and domain reorientations experience accompanying microdeformations. Many applications such as sensors and actuators depend upon the microdeformations of ferroelectrics under external stimuli. The deformations beyond certain limit can result in microcracking of ferroelectric ceramics, causing deterioration of properties. Both intrinsic and extrinsic factors affect the extent of microdeformations. An understanding of these factors and the underlying mechanisms can help in achieving reliable, long term performance of ferroelectric devices.

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Fractography as well as fatigue and fracture of 25 wt% silicon carbide whisker reinforced alumina ceramic composite

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Abstract. Fatigue cracked and fast fractured regions in four-point bend specimens prepared from 25 wt% silicon carbide whisker reinforced alumina composite were examined by scanning electron microscopy. This composite was found to be susceptible to a fatigue crack growth phenomenon similar to that in the case of metallic materials, but with a higher crack growth exponent. In the fatigue region, the alumina matrix failed mainly in a transgranular mode and the whiskers mainly failed with a flat fracture surface but without their pullout. On the other hand, in the fast fracture region, the whiskers failed predominantly by pullout and the alumina matrix failed in a mixed mode with about half in transgranular and the other half in intergranular mode. Thus, to improve the fracture toughness of the material, the grain boundary strength of alumina and the matrix whisker interfacial bonding should be improved. To increase the resistance to fatigue, the fracture strength of the alumina grains should be improved by using finer α -alumina particles and the fatigue strength of the whisker have to be increased by improving the uniformity in distribution of β -SiC whiskers during hot pressing.

Keywords. Alumina; silicon carbide; whiskers; fatigue; transgranular; intergranular; fracture strength.

1. Introduction

Fatigue crack growth rate (FCGR) (Ray and Banerjee 1994; Ray *et al* 1994) and fracture toughness (Krause and Fuller 1990; Ray and Banerjee 1994; Ray *et al* 1994) of 25 wt% silicon carbide whisker reinforced alumina ceramic composite have been studied and reported. Such studies are important since these materials have potential application in the production of structural components used at elevated temperatures, in high efficiency heat engines and heat recovery systems and for making cutting tools to machine special materials. When used in such applications, these ceramic components would often encounter monotonic and cyclic loading which produce crack extension. Therefore, the fractographic features of the fatigue failed samples need to be examined to identify the likely micromechanism of crack advance under monotonic and cyclic loading in this composite. Recently Dauskardt *et al* (1992) studied FCGR and made an extensive fractography of fatigue failed regions in a 15 vol% SiC whisker-reinforced alumina composite. The distinctly identified fractographic features at the low, medium, high ΔK (stress intensity range) fatigue region as well as in the fast fracture region can give clue to the likely mechanisms of fracture in our material.

The four-point bend specimens were sliced, prepared, surface finished and randomized from a 150 mm $\times$ 50 mm $\times$ 12.5 mm preformed billet of 25 wt% silicon carbide whisker reinforced alumina composite material (figure 1a). The details of fabrication of the billet is given elsewhere (Krause and Fuller 1990). The specimens in the

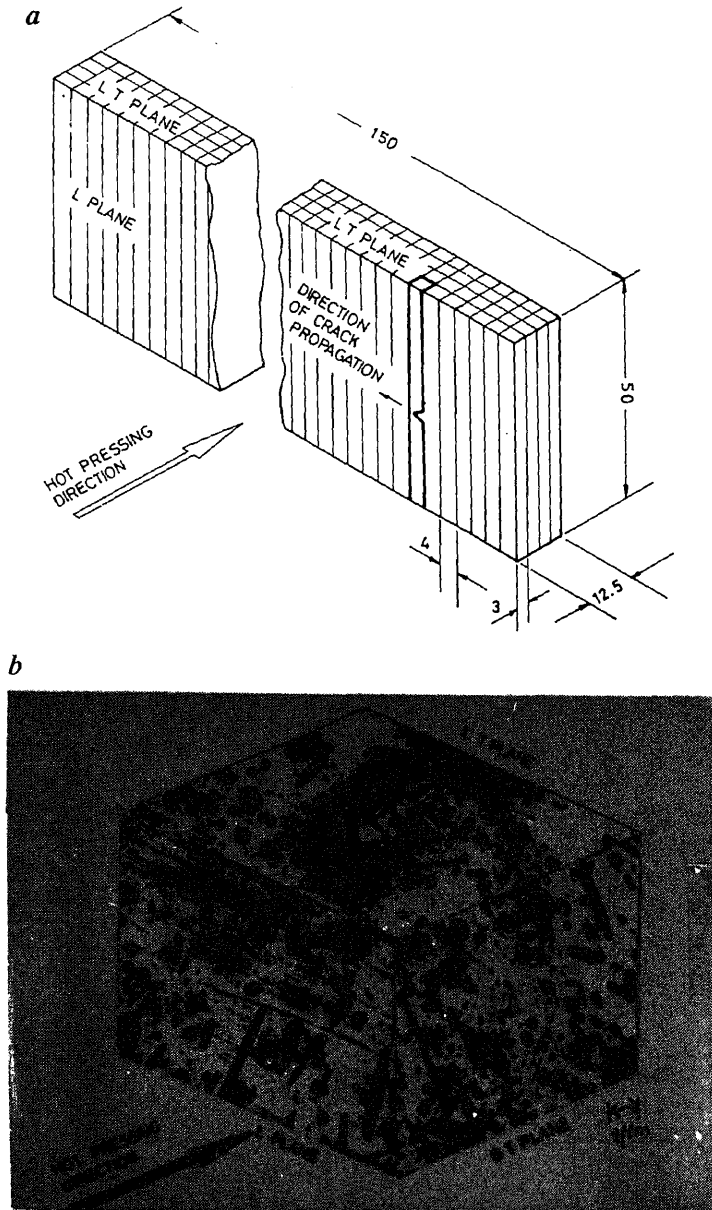


Figure 1. a. Billet prepared from the 25 wt% silicon carbide-alumina composite and b. montage of the microstructures shows distribution of SiC_w along the three planes.

present investigation were supplied to NML by the National Institute of Standards and Technology, USA.

The alumina powder used was of α -type (Krause and Fuller 1990; Ray *et al* 1994). The SiC whiskers had been produced in a carburization process at 1600°C where the sources of silicon and carbon were rice husk ash and rice husk hydrocarbons, respectively (Krause and Fuller 1990; Ray and Banerjee 1994).

The particle size of the alumina powder was less than 1 μm . Normal whisker diameter was 0.1 to 0.25 μm as revealed in the LT plane of the montage of the ceramic composite investigated here (figure 1b). The length of the whiskers varied between 10 to 30 μm (Krause and Fuller 1990).

The scanning electron microscopic (SEM) examination of the fracture surface of the specimens which failed due to premature crack extension during precracking in the conventional bridge fixture (Ray and Banerjee 1994; Ray *et al* 1994) showed that the alumina grain size after fabrication varied between 1 to 6 μm . This confirms that during hot pressing, the alumina underwent substantial grain coarsening, which, in areas where whiskers were absent or there was evidence of pores (figure 2), was as high as 6 μm . However, in other areas, the majority of the alumina grain size was in the range of 2 to 4 μm . This fracture surface indicated an intergranular fracture region in an otherwise transgranular region.

The montage of the ceramic composite revealed 3D-distribution pattern of the whiskers in the longitudinal (L), long transverse (LT) and short transverse (ST) planes. In the L plane, the whiskers appeared to be randomly oriented as the hot pressing direction is perpendicular to this L plane. During hot pressing, whiskers which are not normal to the L plane get further inclined thus producing the random orientation of the whiskers (Ray *et al* 1994). Since maximum material flow occurred along the LT planes during hot pressing, the whiskers get oriented normal to the

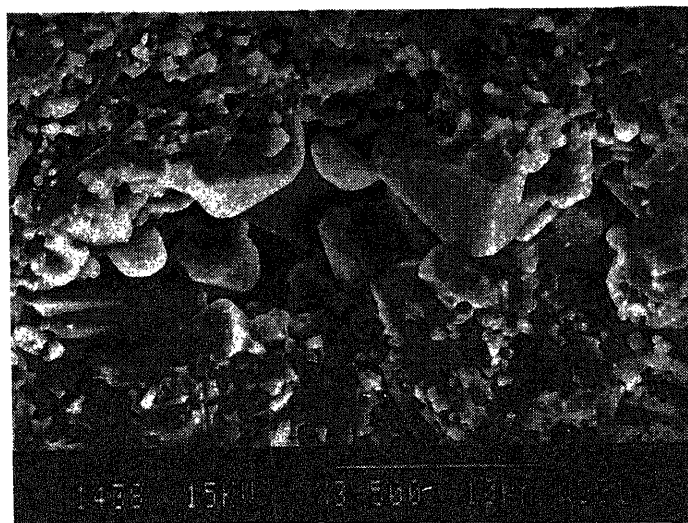


Figure 2. Fracture surface of the composite showing the size and shape of the alumina matrix.

LT plane. In the ST plane, there was a mixture of random orientation as well as normal alignment of the whiskers.

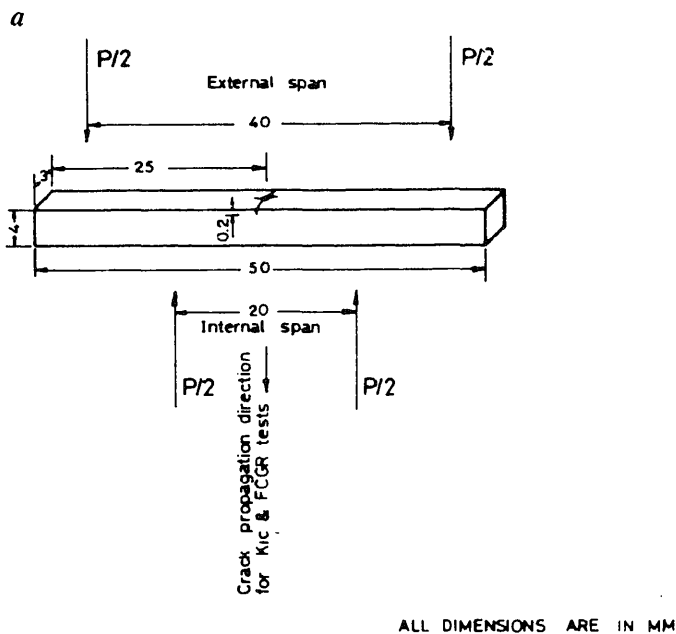
Becher and Wei (1984) concluded in their work that whisker orientation during processing of hot pressed SiC-whisker reinforced alumina leads to anisotropy in both fracture toughness and fracture strength of the composites. In other words, their fracture strengths are limited by the nonuniformity of the distribution of the whiskers i.e. by the ability to disperse the SiC whiskers. They also found that the dispersion of the whiskers improved by using finer alumina powder and hence an increase in the fracture strength of the composite was observed. Nevertheless, they have clearly observed (Becher and Wei 1984; Wei and Becher 1985) that similar to our composite under investigation (figure 1b), the whiskers are preferentially aligned perpendicular to the hot pressing axis. This type of distribution of whiskers suggested that a great deal of rearrangement of whiskers and powder occurred in the initial stage of densification of the composites and/or the matrix material underwent considerable deformation or creep during hot pressing.

The dimensions of the billet and the orientation of the four-point bend specimens ($3\text{ mm} \times 4\text{ mm} \times 50\text{ mm}$) in the billet is given in figure 1a. The $4\text{ mm} \times 50\text{ mm}$ faces were normal to the hot-pressing direction so that both the directions of crack propagation (figure 3) and the crack plane were parallel to the LT plane (figure 1a) and normal to the hot-pressing direction (Krause and Fuller 1990). The $3\text{ mm} \times 50\text{ mm}$ faces of the specimen were parallel to the ST plane.

A Vickers indentation produced at 0.8 kN load at the centre of the ($3\text{ mm} \times 50\text{ mm}$) surface of the specimen acted as the crack starter on half of the four-point bend specimens. On the remaining half, notches were inserted exactly at the centre of the $3\text{ mm} \times 50\text{ mm}$ surface of the specimens with a carborundum wheel to a depth of 0.1 mm. Thereafter, the specimens were subjected to fatigue loading in a servohydraulic test machine MTS-880 (100 kN capacity) to precrack the specimen in an articulated bridge fixture (Ray and Banerjee 1994), till the ratio of crack length to width was 0.65 on the ($4\text{ mm} \times 50\text{ mm}$) surface of the specimen. Precracking was achieved with 100% success with the help of this fixture designed and fabricated at NML, Jamshedpur. Precracking was conducted at a force of 4 to 5 kN, load ratio, $R = 0.1$ and frequency, $f = 20\text{ Hz}$. After this, the fatigue crack growth rate in the specimen was determined at increasing values of stress intensity range, ΔK (figure 4), under normal four-point bend loading (see figure 3) till the ratio of crack length to width was about 0.45–0.5, on the $4\text{ mm} \times 50\text{ mm}$ surface of the specimen. Thereafter, the test to determine the fatigue crack growth rate was terminated and the specimen was subjected to monotonic loading to determine the fracture toughness of the material (Ray and Banerjee 1994) as per ASTM STP 410 (Brown and Srawley 1966). For both FCGR as well as fracture toughness (K_{IC}) tests, a 1 kN load range of the MTS-880 test machine was used. The test frequency was 1 Hz and the loading rate was 0.25 N s^{-1} . Tests were conducted in laboratory atmosphere and at ambient temperature. The fracture toughness testing produced fast fracture. The details of fracture toughness and FCGR tests are given elsewhere (Ray and Banerjee 1994; Ray *et al* 1994).

The fracture surfaces were coated with a thin film of gold (thickness 200°A) prior to SEM examination, in a JOEL JSM 840 A microscope.

The three regions viz. low ΔK corresponding to 0.8 to $1.8\text{ MPa}\sqrt{\text{m}}$; high ΔK corresponding to 2.8 to $3\text{ MPa}\sqrt{\text{m}}$; and, the fast fracture region corresponding to



b

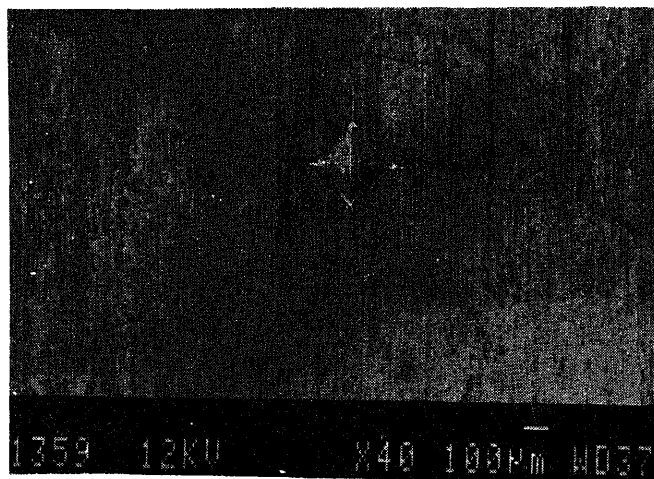


Figure 3. a. Indented and precracked specimen for four-point bend loading, and b. cracks are located at the four corners of indentation.

K_{IC} value of $5.9 \text{ MPa}\sqrt{\text{m}}$, were, at first, identified on the fracture surface at a magnification of $\times 30$ under SEM (figure 5), using the details of the crack growth rate data generated on the specimen, as a guideline. The distinction between the fatigue and fast fracture could, however, be discerned through observation even

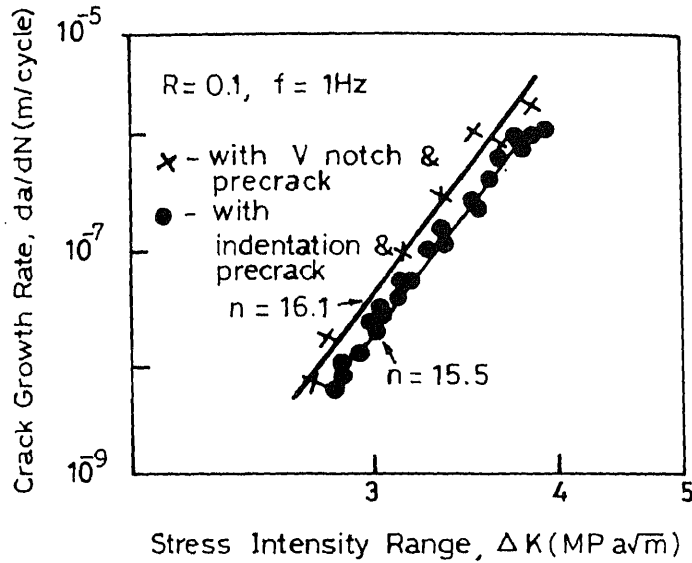


Figure 4. Fatigue crack growth data of 25 wt% SiC reinforced Al_2O_3 composite

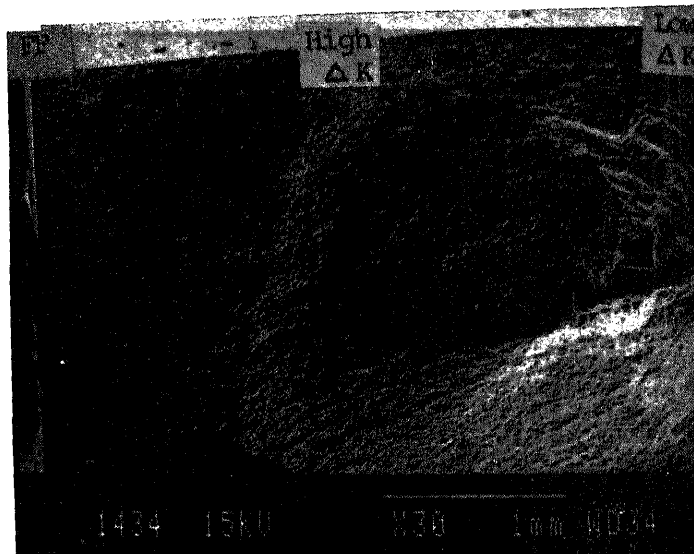


Figure 5. Entire fracture surface. (Right hand side, low ΔK region; middle, high ΔK region; left hand side, fast fracture region (FF)).

with the naked eye. The distinction between the low and the high ΔK fatigue regions was made from the crack length versus the number of cycles data generated during the fatigue loading of the specimen.

Each region was, at first, carefully scanned at low magnification, to identify the general and uniformly distributed features. Thereafter, it was examined at two

different magnifications $\times 4500$ and $\times 7500$, in order to identify the fractographic features and the mechanism of fracture in the low ΔK and the fast fracture regions.

3. Fractographic observations

A summary of the results of the fractographic observations is reported in table 1.

Table 1 states that, at low ΔK (0.8 to 1.8 MPa $\sqrt{m}$), the whiskers failed predominantly by shearing with a flat or square fracture without any visible evidence of necking; this was typical of fatigue fracture (figure 6). However, at high ΔK (2.8 to 3 MPa $\sqrt{m}$), the whisker failed in two different ways: i.e. about 60% of the whiskers failed with a flat fracture and the balance by pullout (figure 7). On the other hand, in the fast fracture region, the whiskers failed predominantly by pullout (figure 8).

Table 1 also reports that the matrix alumina grains failed predominantly through transgranular fracture (figure 9) at low ΔK (0.8 to 1.8 MPa $\sqrt{m}$). In the high ΔK (2.8 to 3 MPa $\sqrt{m}$) region, the matrix failed in a mixed mode wherein about 45% of the alumina grains failed by intergranular and the balance by the transgranular mode, as shown in figure 10. During monotonic loading, the alumina grains in the fast fracture region also failed in a mixed mode with a slightly increased percentage of intergranular (~55%) and the balance by transgranular mode—as shown in figure 11.

It is noteworthy that in the low ΔK region, the crack had frequently branched (figure 12) and deflected (figure 13) while it propagated. Correspondingly, the river pattern markings with steps (figure 14) were also present in the cleavage facets. However, in the fast fracture region, the branching and deflection of the crack were virtually absent.

4. Discussion

Twentyfive weight percent silicon carbide whisker reinforced alumina composite is

Table 1. Fractographic features in the fatigue and fracture regions in a 25 wt% silicon carbide whisker reinforced alumina.

Mechanism of failure		Fatigue		Monotonic fracture (5.96 MPa $\sqrt{m}$)
		low ΔK (0.8 to 1.8 MPa $\sqrt{m}$)	high ΔK (2.8 to 3.0 MPa $\sqrt{m}$)	
Whisker	Pullout (%) vs	5	40	85
	shear (%)	95	60	15
Matrix	Transgranular (%) vs	95	55	45
	intergranular (%)	5	45	55
Crack	o branching			
	o deflection			
	o river pattern	P	A	A

P, present; A, absent.

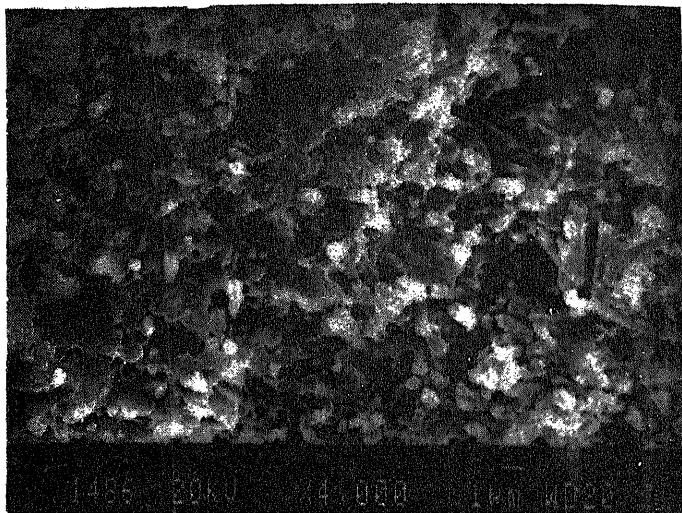


Figure 6. At low ΔK (0.8 to 1.8 $\text{MPa}\sqrt{m}$) region, a majority of the whiskers failed with a square fracture without evidence of large scale pullout.

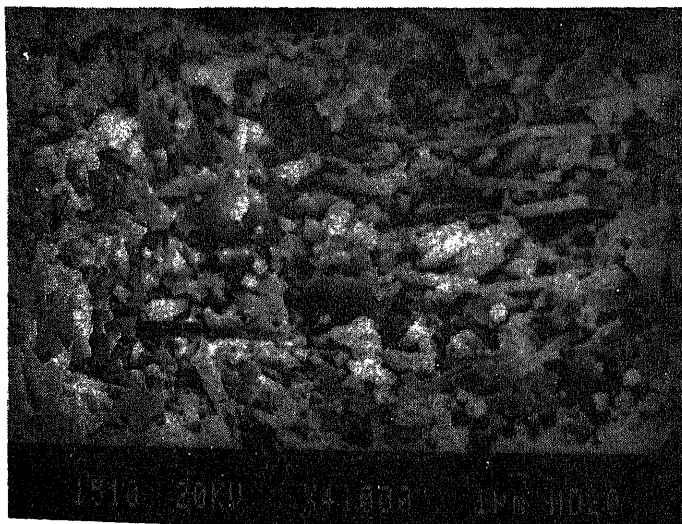


Figure 7. At high ΔK (2.8 to 3 $\text{MPa}\sqrt{m}$) region, the whiskers failed in a mixed mode, i.e. both with a square fracture and also by pullout.

susceptible to a fatigue crack growth phenomenon (Ray and Banerjee 1994; Ray *et al* 1994) as shown in figure 4, which is similar to that in the case of metallic materials, but with a higher crack growth exponent ($n = 15.5$ and 16.1). Figure 4 shows that the FCGR data of this material fits to the usual Paris equation

$$da/dN = A (\Delta K)^n.$$

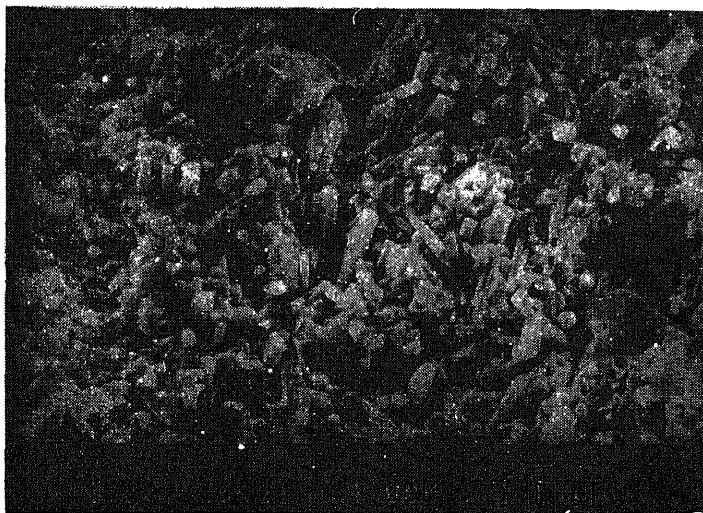


Figure 8. In the fast fracture region ($K_{IC} = 5.9 \text{ MPa}\sqrt{m}$), whiskers failed predominantly by pullout mechanism.

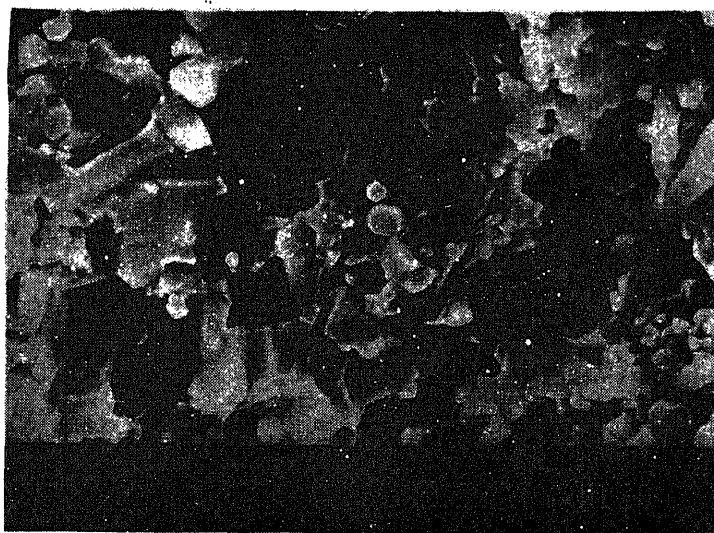


Figure 9. At low ΔK region, the alumina matrix failed predominantly through transgranular fracture.

Recently, FCGR data of 15 volume percent silicon carbide Al_2O_3 ceramic composite has been reported by Dauskardt *et al* (1992) using CT (compact tension) specimens. Comparison of FCGR data of these two composites with different whisker volume and porosity contents have been made and discussed elsewhere (Ray *et al* 1994). The Vicker's indentation when used as a crack starter induces certain amount of



Figure 10. At high ΔK region, the alumina grains failed in a mixed mode i.e. intergranular (~ 45%) and transgranular (~ 55%).



Figure 11. In the fast fracture region (monotonic loading), the alumina grains failed in a mixed mode, i.e. intergranular (~ 55%) and transgranular (~ 45%).

residual stresses in the material (Marshall and Lawn 1977; Ikuma and Virkar 1984; Ponton and Rawlings 1989). Residual stresses present in the parent sample due to grinding while fabrication and ahead of a V notch as well as indent along the crack propagation direction were determined using a X-ray stress analyzer, (AST-X2001). The details of residual stress measurement have been discussed



Figure 12. Crack branching in the low ΔK region.

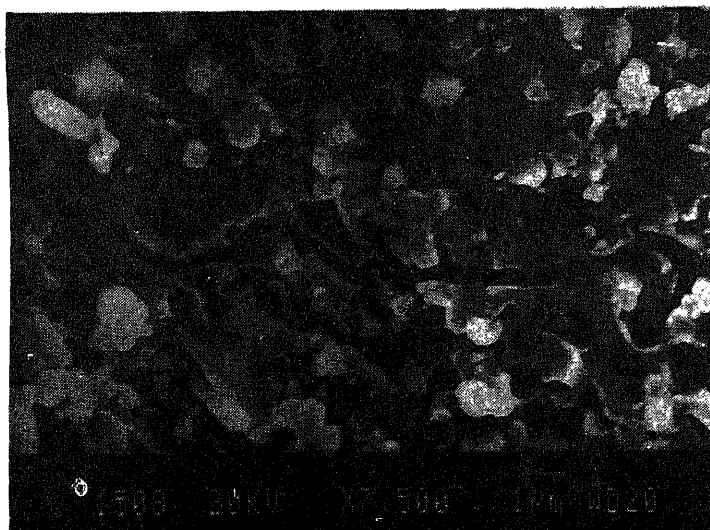


Figure 13. Crack deflection in the low ΔK region.

elsewhere (Ray and Banerjee 1994). If these stresses are compressive in nature, it would expect to retard the fatigue crack growth rate of the material. This type of behaviour was clearly demonstrated in our composite (figure 4), where the FCGR at a given ΔK for a V notch with precrack as a crack starter was slightly high compared to that in the case of indentation with precrack as a crack starter. Table 2 reveals that although the nature of residual stresses ahead of the advancing crack,

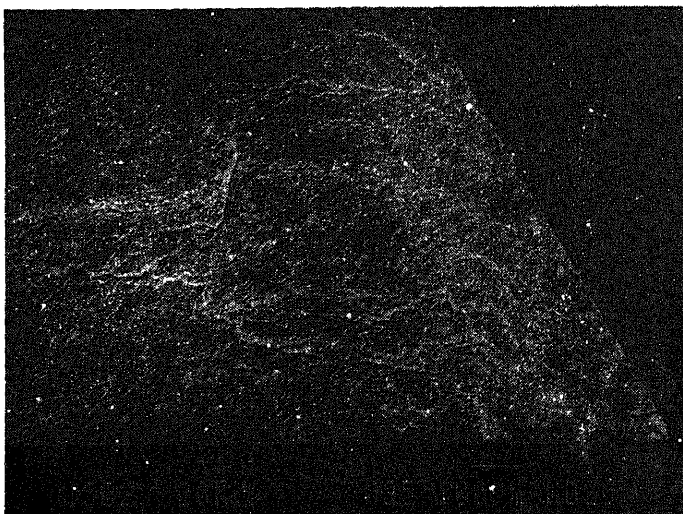


Figure 14. River pattern marking with steps in the low ΔK region (YZ, modulation SEM image).

Table 2. Residual stresses present in the ceramic composite.

Material	Specimen type	Residual stresses measured in AST-X 2001 (MPa)
25 wt% SiC	Parent	325.00 ± 0.4
reinforced Al_2O_3	Ahead of indent	282.8 ± 0.8
ceramic composite	Ahead of notch	396.7 ± 0.9

were tensile for both notched and indented sample, relatively certain amount of compressive residual stresses were induced in the latter compared to the notched samples. The process of inserting a V notch in the specimen therefore has induced a considerable amount of tensile residual stresses. This is indicative of a higher n value (16.1) with a slight higher crack growth rate at a given ΔK in figure 4 compared to that of indented and precracked four-point bend specimen. The respective A values of Paris law equation have been given in table 3 (Ray and Banerjee 1994).

Fracture toughness values determined by using both types of crack starters and as reported in table 4 (Ray and Banerjee 1994), show that the average K_{IC} values obtained from indentation as a crack starter in indented and precracked specimens were $\sim 7.77\%$ higher than those obtained from V notched and precracked specimens. This possibly is attributed to the presence of less tensile residual stresses or in other words more compressive residual stresses in the notched sample compared to the residual stresses present in the indented sample, as can be confirmed from table 2. It should be noted that the term compressive is used only in a relative

Table 3. Paris law constants (A and n) from FCGR data.

Material	Type of specimen	A [m/cycle (MPa√m) ⁻ⁿ]	N
25 wt% SiC reinforced Al ₂ O ₃ ceramic	Notched and precracked	5.579×10^{-16}	16.1
	Indented and precracked	3.4×10^{-15}	15.5

Table 4. Fracture toughness K_{IC} determined by the ASTM procedure at NML.

Material	Fracture toughness K_{IC} in MPa√m		
	NML		NIST
	Notched and precracked	Indented and precracked	Indentation
25 wt% SiC	5.44	6.1	5.35 ± 0.17
reinforced Al ₂ O ₃	5.63	5.8	
ceramic composite	5.52	6.0	
	5.53 ± 0.05 average	5.96 ± 0.07 average	

sense in order to delineate from the tensile residual stresses already in the parent specimen as well as in the specimen with notch. The large difference in toughness between indented and precracked specimens (table 4) and the one reported by NIST, could primarily be accounted for the difference in crack tip loading rates. Fuller has represented K_R values from the expression

$$K_R = 5.35 (C/18.1 \mu\text{m})^{0.08},$$

where C is the crack length and K_R is a parameter which describes the fracture resistance for a R -curve material. Using this relation one could derive an indentation-crack-length toughness (Krause and Fuller 1990). In R -curve type materials, the toughness varies with crack extension, so that if one attempts to measure the toughness with a procedure that ignores this as do most of the earlier indentation techniques, one would find that measured toughness depends on indentation loads.

Since the manner of failure of the whiskers and the α -alumina grains were entirely different in the low ΔK fatigue and the fast fracture regions, the scheme of crack growth under these two conditions are discussed separately, to focus on their contradistinctions.

4.1 Low ΔK fatigue region

During fatigue loading at the low ΔK regions, when $K_c = 1.8$ to $2 \text{ MPa}\sqrt{\text{m}}$ – the alumina grains of the matrix failed mainly by transgranular cleavage with frequent crack branching and crack deflection. Also, the cleavage facets revealed river pattern

the crack tip, were not large enough to promote intergranular fracture.

At low ΔK , the amount of crack extension is very low. So even though the energy dissipated per cycle is low, the number of cycles and the cumulative energy required for a given amount of crack extension is quite significant and can thus account for the higher surface area required for the various features encountered like crack branching, river pattern and steps.

At low ΔK fatigue, the whisker could fail in three different modes: (i) pullout, (ii) tensile fracture and (iii) fatigue. Table 1 shows that only a few of the whiskers failed due to pullout at low ΔK fatigue. This naturally indicated that the maximum traction forces generated ahead of the crack tip during the low ΔK fatigue was not adequate to produce a pullout. Thus, it is likely that the whiskers continue to bridge the crack even after some of the surrounding alumina grains had failed by transgranular cleavage. Therefore, under these circumstances, the whisker could fail due to tensile fracture or fatigue.

One might rule out the possibility of tensile fracture if one had examined the relative values of strength and Young's modulus reported by Fisher *et al* (1991) and Ray *et al* (1991). The fracture strength of the whisker is about 6.5 to 7 times higher than that of alumina. Accordingly, the tensile fracture of the whisker was unlikely if the traction forces ahead of the crack tip were to be distributed in proportion to the relative cross-sections of the whisker and alumina in the plane of the crack. Even if the whiskers were to carry the major part of the traction forces ahead of the crack tip, the high traction forces would produce failure by pullout rather than by tensile fracture, as was observed in the fast fracture region where K_{IC} values and consequently the traction forces, were high.

Since the possibility of large scale failure by pullout or tensile fracture was discounted, whiskers were most likely to fail by fatigue. At low ΔK , the whiskers which had bridged the crack after the surrounding alumina grains had failed by cleavage, would continue to experience fatigue loading, then failed with a square fracture which is typical of fatigue. The fatigue failure of the silicon carbide whisker under such circumstances, could be significantly influenced by the stacking fault such as is reported in figure 15 (Ray *et al* 1991), since such fault could be responsible for nucleating the fatigue crack. However, this aspect needs careful study.

Since cleavage of the α -alumina grains occurred probably before the whiskers (located mainly at the grain boundaries) had failed, it was necessary to improve the fatigue resistance of the α -alumina grains. This apart, the dislocation pile-up model (Kingery *et al* 1976) would obviously indicate that the cleavage failure of α -alumina could be prevented through the refinement of alumina grains in the aggregate structure. The size of alumina grains varied between less than 1 to 6 μm . In this context, one should note that one could obtain higher resistance to low ΔK fatigue, if ultra-fine or nano-size alumina grains such as that produced by the sol-gel technique were to be used to fabricate this composite.

A schematic view of crack propagation mechanism is represented in figure 16a. It illustrates that at low ΔK fatigue, the matrix failed predominantly by transgranular fracture and the advancing crack frequently branched and tilted and twisted in its course of deflection. Since the whiskers were predominantly located at the grain boundaries and the crack propagation along the grain boundary at low ΔK fatigue



Figure 15. TEM of β -SiC whisker showing stacking fault by dark field and bright field techniques (Ray *et al* 1991).

was negligible, the possibility that the crack would encounter these whiskers as it advances would be rather low. Only a few of those whiskers which had bridged the crack with an orientation normal to the advancing crack plane, could fail by pullout. The other whiskers were likely to fail by directly experiencing fatigue loading. This could explain why at low ΔK fatigue, a majority of the whiskers failed with a square fracture and without pullout.

4.2 Fast fracture region

During the fast fracture under monotonic loading such as during the fracture toughness testing, some of the α -alumina grains of the matrix failed by intergranular fracture; the others failed by transgranular cleavage. The value of K_{IC} during such monotonic loading was $5.9 \text{ MPa}\sqrt{\text{m}}$. At such values of K_{IC} , the traction force generated ahead of the crack tip, was adequate to produce the intergranular failure in those grains which were favourably oriented with respect to the direction of the traction force. Debonding and pullout of those whiskers at the fractured grain boundaries would therefore occur.

It is difficult to summarize from the fractographic features as to which of these, i.e. transgranular cleavage or intergranular fracture occurred, at first, under monotonic loading.

After some of the grains had failed through the intergranular mode, the other neighbouring grains which were less favourably oriented or which were strongly anchored by the whiskers across the grain boundaries, failed through transgranular cleavage.

The pullout of the whiskers could be avoided if the whisker alumina interfacial strength was improved or if finer and more numerous whiskers and also finer α -alumina particles were used in fabricating the composite. Similarly, the intergranular fracture could be avoided by strengthening the boundaries.

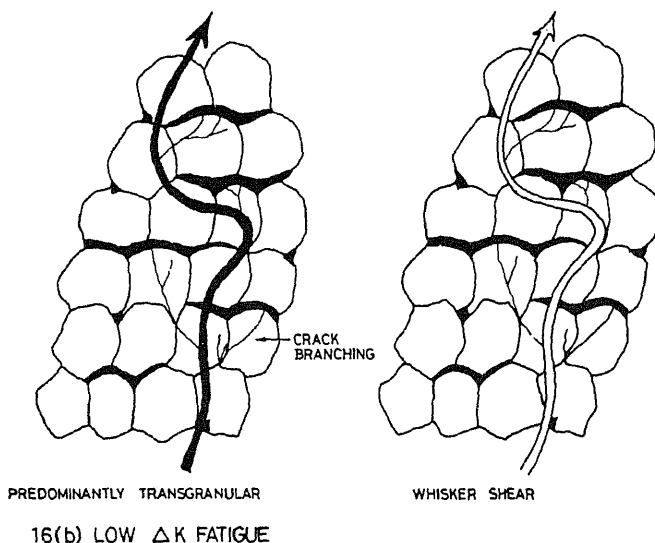
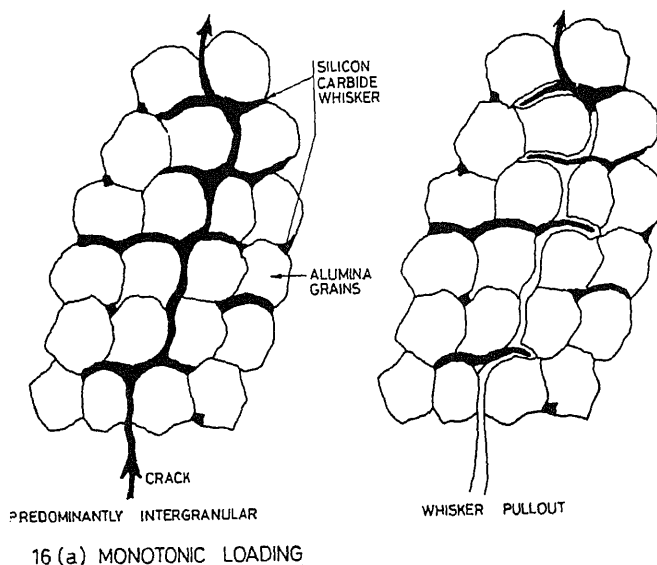


Figure 16. Schematic of the crack propagation during monotonic and cyclic loading.

As illustrated schematically in figure 16b, the fracture due to monotonic loading showed a substantial amount of intergranular failure of the matrix and pullout of the whiskers. Crack deflection, branching and the characteristic river pattern marking with steps, were absent in this region.

The matrix failure was predominantly intergranular. Nevertheless, the whiskers are located mainly at the grain boundaries. Therefore the probability of the advancing crack front interacting with the whiskers was extremely high. The whiskers tending to bridge the advancing crack quite frequently would therefore get debonded and pullout—which is schematically illustrated in figure 16b—were located at the grain boundaries only. Therefore, the whiskers would tend to bridge the advancing crack

quite frequently and, therefore, these would get pulled out which is schematically illustrated in figure 16b. This justifies the fact that during the monotonic fracture, failure of whiskers by the pullout mechanism was frequently observed in the fractograph.

During fatigue loading at high ΔK , mechanism of fracture was an intermediate situation between the two extreme cases, i.e. between the monotonic fast fracture and that of the low ΔK fatigue fracture.

Since the ceramic material is often expected to survive both monotonic and fatigue loading, one could make the following general observations based on the scheme of crack growth under the two conditions as discussed above.

To prevent fracture failure of this ceramic material under monotonic loading, its microstructural features would have to be strengthened to avoid intergranular fracture of α -alumina and the pullout of the whisker. This requires that the grain boundary strength of α -alumina and the whisker-matrix interfacial strength should be increased. Similarly, to retard crack extension during low ΔK fatigue, intergranular cleavage fracture of α -alumina grains and fatigue failure resistance of the silicon carbide whiskers should be improved, possibly by using finer α -alumina powder (Becher and Wei 1984; Wei and Becher 1985) and by improving the uniformity of distribution of whiskers in the matrix during hot pressing (Becher and Wei 1984, 1985) of the whiskers.

5. Conclusions

The following conclusions were arrived at from the results of this study.

- (i) 25 wt% SiC reinforced Al_2O_3 ceramic composites are susceptible to a crack growth phenomenon which is similar to that in the case of metallic materials but with a higher exponent.
- (ii) There was 100% success in pre-cracking ceramic specimens with the help of an articulated bridge fixture. Between indented with precrack and V notched with precrack four-point bend specimens, the use of indentation as a crack starter influenced the K_{IC} values mainly and the fatigue crack growth rate to some extent, due to the presence of certain amount of compressive residual stresses ahead of the advancing crack.
- (iii) The micro-mechanism of fracture of a 25 wt% silicon carbide whisker reinforced alumina composite when loaded in fatigue was quite different from that when loaded monotonically. Consequently, the fractographic features in the two instances of loading were significantly different.
- (iv) When loaded in fatigue, the alumina matrix failed in a transgranular mode and the whiskers failed by producing a flat fracture but without their pullout.
- (v) When loaded monotonically, the whiskers predominantly failed by pullout and the alumina matrix failed in a mixed mode with about half in transgranular and the other half in intergranular mode. Whereas the grain boundary strength of α -alumina and the whisker-matrix interfacial bonding should be increased to produce increased resistance to failure under monotonic loading. The fatigue failure resistance could be improved by improving the cleavage strength of the α -alumina grains i.e. by using finer α -alumina particles and by increasing the fatigue strength of the whiskers by improving the uniformity in the distribution of β -SiC whiskers during hot pressing.

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Electrokinetic behaviour and dispersion characteristics of ceramic powders with cationic and anionic polyelectrolytes

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Abstract. Three different ceramic powders, viz. alumina, zirconia and silicon nitride were dispersed using two polyelectrolytes, one cationic (Betz 1190) and the other anionic (Darvan-C). All powders examined during the study could be well dispersed only under conditions of polymer dosage and pH such that the working pH is at least 2 pH units away from the pH_{IEP} of the powder-dispersant combination. The shift in the isoelectric point (IEP) of the powders were determined through electro-acoustic measurements on 1% volume suspensions. Specific free energy of interaction were also computed using a model based on the electrical double layer theory of surfactant absorption.

Keywords. Electrokinetics; dispersion; alumina; zirconia; silicon nitride; polyelectrolytes; electroacoustophoresis; Darvan-C; Betz 1190.

1. Introduction

Colloidal processing techniques are considered to be most promising in the preparation of advanced ceramic products with improved mechanical and electrical properties, partially as a consequence of achieving better homogeneity in the green bodies formed through colloidal routes (Lange 1989). Adequate control of the rheology of concentrated particulate slurries is crucial for the success of such processing methods. For example, the optimum performance of processes like spray drying, injection moulding, slip and tape casting and pressure filtration is dependent on the preparation of a slurry having maximum volume fraction of solids yet exhibiting minimum viscosity (Leong *et al* 1991). The rheological control is accomplished in practice with the addition of certain reagents (inorganic, organic and polymeric surfactants) known as dispersants (Chou and Lee 1989; Bleier and Westmoreland 1991; Bleier 1992; Bleier *et al* 1992). The dispersants adsorb at the solid/liquid interfaces and appropriately alter the surface properties of the colloids facilitating desired dispersion. Currently, these surfactants are selected by trial and error, their dosages arrived at based on experience and rules of thumb (Calvert *et al* 1986). There thus exists a need to develop the science of dispersants design i.e. a methodology to systematically design and/or select dispersants for the specific problem at hand based on our scientific understanding of the surface forces between particles.

Certain trade names and company products are mentioned in the text or identified in illustrations in order to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by the authors and their respective institutes nor does it imply that the products are necessarily the best available for the purpose.

The stability of a dispersed colloid system can be quantitatively described by the classical DLVO (Derjaguin, Landau, Verwey and Overbeek) theory which considers two types of long range forces between colloidal particles; viz. the van der Waals London attractive forces and the electrical double layer (attractive or repulsive depending upon the surface charge) forces (Hunter 1981; Israelachvili 1992). The adsorption of charged surfactant species (inorganic, organic or polymeric) at the interfaces leading to repulsive interaction can thus be utilized to achieve stability, i.e. electrostatic stabilization of colloids (Hogg *et al* 1966). Another mode of achieving colloidal dispersion, i.e. through the adsorption of relatively long chain polymers, is called steric stabilization. The protective layer of the polymer on the surface gives rise to steric repulsion leading to enhanced colloidal stability (Napper 1983).

It is important to note that electrostatically stabilized dispersions are kinetically stable, but are very sensitive to the presence of electrolytes. With increasing ionic strength, the electrical double layer repulsion is reduced causing coagulation. On the other hand, sterically stabilized dispersions are thermodynamically stable and are relatively more tolerant of the electrolytes. In dispersions stabilized by polyelectrolytes (e.g. polyacrylic acid), both the mechanisms, viz. the electrostatic as well as the steric, are important. Such dispersants are also called electrosteric stabilizers (Sung and Piirma 1994).

The purpose of the ongoing research in our laboratories is to evaluate the effectiveness of various commercial dispersants in ceramics processing as well as to understand the underlying mechanisms of dispersion, particularly in concentrated slurries. It is envisaged that these efforts would enable us to develop a scientific methodology for the design of tailor made dispersants for the specific problems faced by the industry. We present in this paper, the results of our work on the dispersion of ceramic suspensions using two kinds of polyelectrolytes (anionic and cationic). A model based on electrical double layer theory is also presented so as to quantitatively compare the specific interaction between the adsorbing polymer and the colloidal surface.

2. Experimental

2.1 Materials

Three powder samples, viz. alumina, stabilized zirconia and silicon nitride were selected for this study. The physical and surface chemical characteristics of the powders are summarized in table 1.

Two polyelectrolyte dispersants, viz. Darvan-C (ammonium polymethacrylate), an anionic polymer obtained from Vanderbilt Co., USA and Betz 1190 (quaternized polyamine epoxy chlorohydrin) a cationic polymer supplied by Betz Co., USA, were used in this study. Both the polymers had an average molecular weight around 10,000. All polymer dosages are represented in parts per million (ppm), i.e. mg of polymer per unit volume of solution.

2.2 Methods

Matec ESA 8000 system (Matec Applied Sciences, USA) was used for electroacoustic

Table 1. Physical and surface chemical characteristics of powder samples.

Powder	Source	BET surface area* (m ² /g)	Average particle size d_{50}^{**} (microns)	PZC [†] (pH)
Alumina (A-16)	Alcoa, USA	9.3	0.38	9.9
Zirconia (SY5.2)	Z Tech, Australia	14.9	0.21	6.65
Silicon nitride (SNE-10)	Ube, Japan	10.1	0.4	6.5

*Micromeritics surface area-pore volume analyzer; **Laser light scattering instrument, HORIBA, LA-9000; †Matce ESA 8000.

measurements on the powder suspensions (0.5% or 1% by volume). Electrokinetic sonic amplitude (ESA) as a measure of the surface charge on the particle was determined following a standard procedure, as described in detail earlier (Hackley *et al* 1993). The mobilities are presented in the form of ESA (MPa.m/v), measured during experiments. All the measurements were carried out in 10^{-3} M sodium nitrate solutions at room temperature. The suspensions were prepared in deionized water by ultrasonic dispersion. pH adjustments were made with the help of analytical grade nitric acid and sodium hydroxide solutions.

The extent of dispersion under given conditions was determined by measuring the particle size distribution of the powder. Under the conditions of perfect dispersion with no coagulated aggregates present in the suspension, the average particle size for the sample (d_{50}) coincided with the average particle size of the powder. An increase in d_{50} of the powder indicated the presence of aggregates (usually a bimodal particle size distribution was also observed under these conditions) and hence unsatisfactory dispersion. All measurements were carried out at a concentration of 5% solids by weight (1 g solid powder in 20 ml solution); the suspension prepared by ultrasonic dispersion and the size distributions measured by HORIBA LA-900, a laser scattering particle size analyzer (Premachandran and Malghan 1994).

3. Results and discussion

The isoelectric point (IEP) for alumina was found to be at pH 9.9 in the absence of dispersant. With increasing addition of anionic dispersant Darvan-C, the IEP of the powder measured through ESA measurements was found to shift to more acidic pH values as shown in figure 1.

The IEP of zirconia powder was measured to be at pH 6.65. In the presence of a cationic dispersant, Betz 1190, the IEP of zirconia powder was observed to shift to more alkaline pH as illustrated in figure 2.

The IEP of silicon nitride powder was observed to occur at pH 6.5. The electrokinetic behaviour of the powder in the presence of anionic (Darvan-C) and cationic (Betz 1190) depresants shown in figure 3 exhibits trends very similar to alumina and zirconia powders. The shift in IEP was towards acidic pH with an addition of anionic polymer and towards alkaline pH in the presence of a cationic polymer.

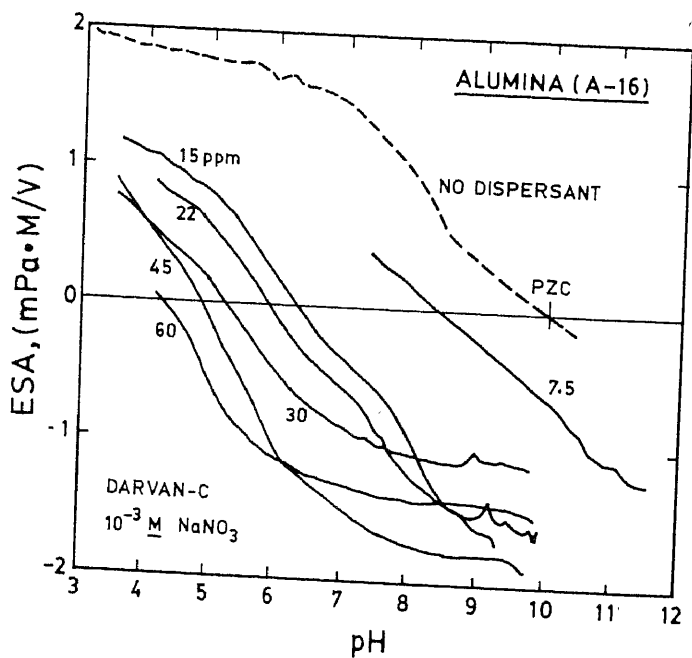


Figure 1. Electro-acoustic measurements of alumina suspensions (1 vol.%) in presence of Darvan-C.

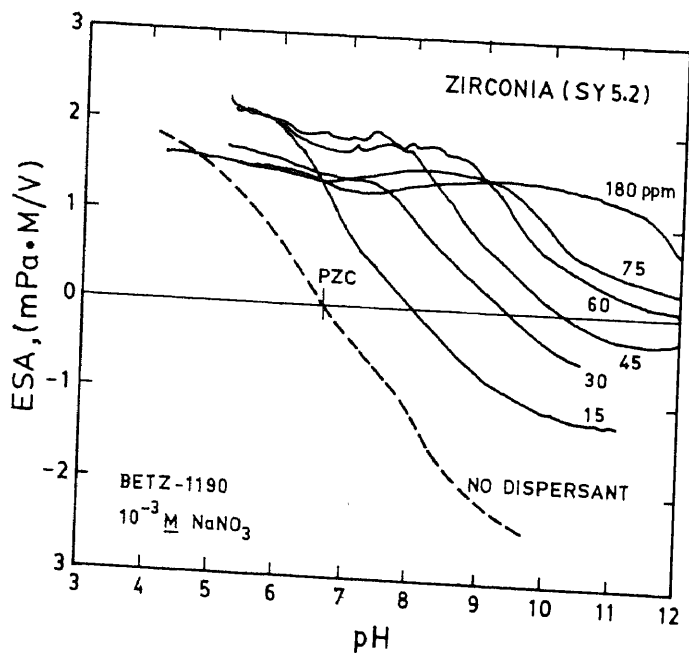


Figure 2. Electro-acoustic measurements on zirconia suspensions (1 vol.%) in presence of Betz 1190.

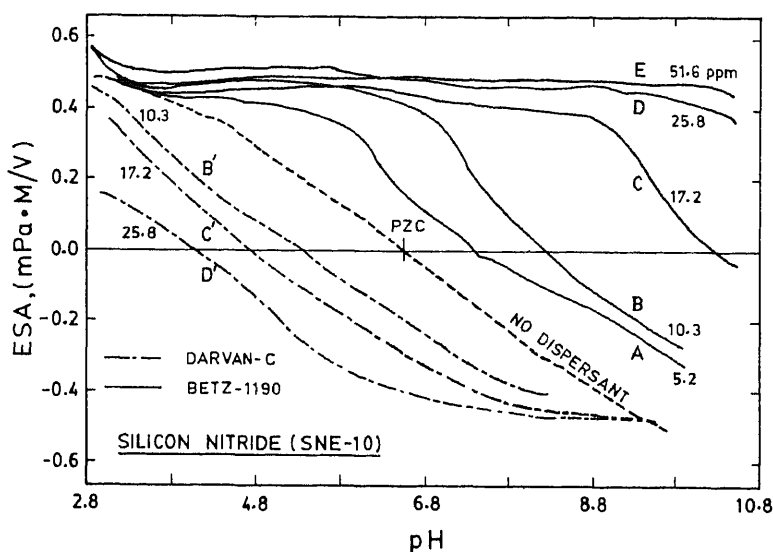


Figure 3. Electro-acoustic measurements on silicon-nitride suspensions (0.5 vol.%) in presence of Darvan-C and Betz 1190.

The corresponding dispersion experiments carried out in order to determine the optimum conditions for best dispersion indicated that at dispersant dosages and under pH conditions where the powder is close to its IEP, the dispersion was unsatisfactory. Some of the illustrative results are summarized in table 2.

The results indicated that for good dispersion, indicated here by the mean size being close to the mean size of the powder, the polymer dosage and pH needs to be controlled such that the difference between the working pH and pH_{IEP} of the powder (with or without dispersant as the case may be) is at least 2 pH units. Under conditions close to IEP, irrespective of the polymer added, the suspension was always observed to coagulate. For example, in presence of Darvan-C, an anionic dispersant at dosages above 75 ppm, both alumina and zirconia exhibited an IEP of pH 4. It is impossible, therefore, to disperse these powders with Darvan-C. In fact, both these powders can be dispersed well at pH 4 without Darvan-C rather than in its presence. Addition of Darvan-C shifts the IEP to more acidic pH causing reduction in the repulsive interaction and hence deterioration in dispersion. This example clearly illustrates the role of electrostatic interactions in the dispersion of powders. One would expect a polymeric dispersant like Darvan to function primarily through steric stabilization mechanism and hence not be sensitive to pH. But it is not so. The absence of electrostatic repulsion at pH close to IEP leads to aggregation—the steric interactions appear to be inadequate to overcome the van der Waals attraction.

It is thus concluded that a judicious combination of dispersant dosage and pH condition (at least 2 pH units away from IEP) is essential for achieving dispersion of powders using commercial polyelectrolytes. It is therefore recommended to establish the IEP of the slurry in presence of the dispersant under consideration before attempting evaluation of its efficacy. The results indicated that for alumina,

Table 2. Correlation of the extent of dispersion as measured through d_{50} , the mean size.

System	pH _i	(pH _i -pH _{IEP})*	Dispersion	
			d ₅₀ (μm)	Remarks
Alumina (A-16)				
No dispersant (pH _{IEP} 9.9)	4	5.9	0.38	W
	10	1.1	3.59	N
With 75 ppm Darvan-C (pH _{IEP} 4.5)	4	0.5	4.18	N
	10	5.5	0.38	W
With 150 ppm Betz 1190 (pH _{IEP} > 10)	4	> 6	0.39	W
	8.1	> 2	0.38	W
Zirconia (SY 5.2)				
No dispersant (pH _{IEP} 6.65)	4	2.7	0.21	W
	4	~ 0	9.8	N
With 75 ppm Darvan-C (pH _{IEP} 4)	7.4	3.4	0.21	W
	9.1	5.1	0.21	W
	6.3	> 5.7	0.21	W
Silicon nitride (SNE-10)				
With 25 ppm Darvan-C (pH _{IEP} 4.1)	9	4.9	0.4	W
With 25 ppm Betz 1190 (pH _{IEP} > 12)	9	> 3	0.4	W

*The electrical double layer repulsion increases with increasing (pH_i-pH_{IEP}). W, Well dispersed; N, No dispersion.

zirconia and silicon-nitride powders, a cationic polymer like Betz could be used quite effectively. With Darvan-C, on the other hand, the dispersion was possible only at alkaline pH.

4. Electrokinetics of dispersant adsorption

Another important observation worth noting in the results presented in figures 1 to 3 is the characteristic shift in the isoelectric point observed with addition of dispersants. The magnitude of this shift in IEP is a measure of the affinity of the adsorbing dispersant for powder surface. Following the electrical double layer theory of surfactant adsorption (Somasundaran and Fuerstenau 1966; Wakamatsu and Fuerstenau 1968; Osseo Asare and Fuerstenau 1973; Hunter 1981; Pradip and Fuerstenau 1983), Pradip (1988) recently established an explicit relationship between the characteristic shift in IEP and the concentration of the chemisorbing surfactant in solution. Using this equation, it is possible to compute the specific free energy of interaction for each powder-dispersant combination and to thus compare the relative efficiency of various dispersants for a particular powder under consideration. An attempt has been made in this section to confirm the validity of this relationship.

Assuming Stern-Grahame type of adsorption isotherm for the dispersants adsorbing at a ceramic powder surface,

$$\theta/1 - \theta = c/55.5 [\exp(-\Delta G_{\text{ads}}^0/RT)], \quad (1)$$

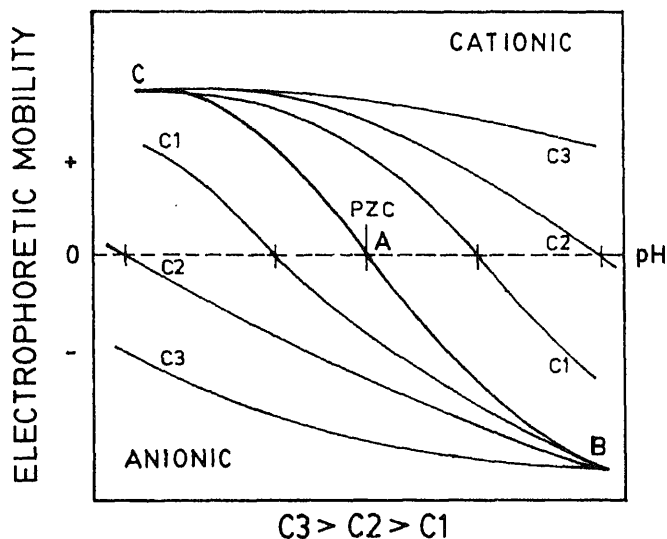
where $\theta = (\Gamma_s/\Gamma_m)$ is the fractional surface coverage at equilibrium concentration in moles/litre in solution. Γ_s and Γ_m represent the adsorption density in mole/cm² at concentration c and at saturation (monolayer coverage) level respectively. Furthermore, the cross-sectional area of dispersants is assumed to be around 20–25 Å² which means that Γ_m is 7×10^{-10} mole/cm². The inner layer capacity of the double layer at the ceramic surface is assumed to be 20 microfarad/cm². Following Pradip (1988), one can then derive that

$$\Delta \text{pH}_{\text{IEP}} = 1.0396 C_0 \exp(-\Delta G_{\text{sp}}^0/RT), \quad (2)$$

where $\Delta \text{pH}_{\text{IEP}}$ is the shift in the iso-electric point at the dispersion concentration C_0 and $-\Delta G_{\text{sp}}^0$ represents the corresponding specific energy of interaction between the ceramic powder surface and the dispersant. R and T are the standard gas constant and the temperature in °K.

The assumptions enumerated above are reasonable for the system under consideration. More precise calculations can, of course, be carried out if the data regarding the adsorption isotherm and the cross-section area of the adsorbing molecules is also available.

The electrokinetic behaviour of a solid surface in the presence of an adsorbing surfactant (cationic or anionic) can be schematically described as shown in figure 4. For a solid surface having an IEP at A (also known as the point of zero charge (PZC)), i.e. IEP in absence of the dispersant, the IEP will shift towards more



$$\Delta \text{pH}_{\text{IEP}} = 1.0396 C_0 \exp \left(-\frac{\Delta G_{\text{SP}}^0}{RT} \right)$$

$$\text{Where } \Delta \text{pH}_{\text{IEP}} = \text{pH}_{\text{IEP}}^{(\text{Ci})} - \text{pH}_{\text{PZC}}$$

Figure 4. A schematic explaining the effects of anionic and cationic dispersants on the isoelectric point (IEP) of powders.

presence of dispersant exactly follows the behaviour observed in its absence. This is due to the fact that under these conditions the specific energy of interaction (attractive) between the adsorbing surfactant and the surface is exactly counter-balanced (equal and opposite) by the electrostatic energy of repulsion between the similarly charged surface and the adsorbing molecule. Hence, the adsorption is zero. At points B and C,

$$\Delta G_{sp}^0 = -\Delta G_{elec}^0,$$

and thus

$$\Delta G_{ads}^0 = \Delta G_{sp}^0 + \Delta G_{elec}^0 = 0.$$

The specific energy of interaction ΔG_{sp}^0 for each of the dispersant powder combination studied during this work was computed following (2). The results are presented in table 3 and figure 5 indicating confirmation of our assumptions.

A log-log plot for pH_{IEP} vs the concentration in solution should exhibit a slope of unity as per (2). As illustrated in figure 5, except for a slight discrepancy in case of alumina Darvan-C at higher dosages, the proposed equation fits the data remarkably well. The specific interaction energies thus computed were found to be between -13.5 to $-14.7 RT$ (8-9 Kcal/mole) for all the four powder-dispersant combinations investigated as part of this work. It suggests that both Darvan-C

Table 3. ΔG_{sp}^0 , as estimated by (2), assuming the dispersant molecular weight for both Darvan-C and Betz 1190 to be 10,000.

System	C_0 (ppm)	ΔpH_{IEP}	ΔG_{sp}^0 (RT units)
Alumina (A-16)			
Darvan-C	7.5	1.6	-14.5
	15	3.7	-14.7
	22.5	4.1	-14.4
	30	4.7	-14.2
	45	5.1	-13.9
	60	5.7	-13.7
Zirconia (SY 5-2)			
Betz 1190	15	1.35	-13.7
	30	2.75	-13.7
	45	3.55	-13.5
	60	5.55	-13.7
Silicon nitride (SNE-10)			
Darvan-C	10.3	1.2	-13.9
	17.2	1.8	-13.8
	25.8	2.4	-13.7
Silicon nitride (SNE-10)			
Betz 1190	5.2	0.8	-14.2
	10.3	1.8	-14.3
	17.2	3.8	-14.6

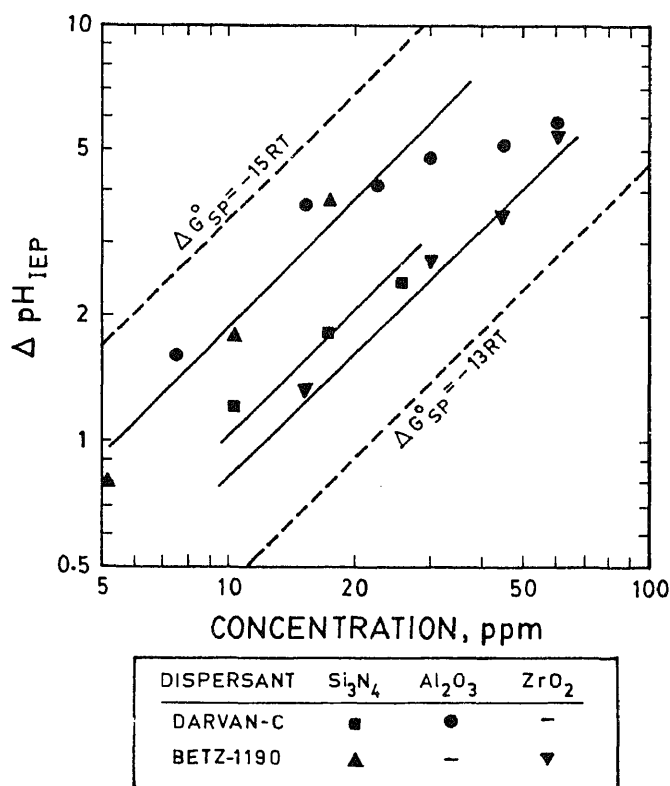


Figure 5. A plot of the shift in isoelectric point $\Delta\text{pH}_{\text{IEP}}$ for alumina, zirconia and silicon nitride suspensions as a function of concentration in solution (2). The dotted lines represent the relationship predicted by (2) for varying specific energies of interaction ΔG_{sp}^0 .

(essentially containing carboxylic acid functional groups) and Betz 1190 (containing amine functional groups) adsorb quite strongly at alumina, zirconia and silicon-nitride surfaces.

5. Conclusions

The dispersion of three different ceramic powders was studied using two polyelectrolytes, one cationic (Betz 1190) and the other anionic (Darvan-C). The results strongly indicated the importance of electrical double layer repulsive interactions in achieving dispersion of ceramic powders. It was observed that the steric forces alone are not sufficient to overcome the attractive van der Waals forces, under pH conditions close to the pH_{IEP} of the powder-dispersant combinations, at least for the low molecular weight polymeric dispersants investigated during this work. The working pH must therefore be at least two pH units away from the pH_{IEP} of the powder-dispersant combinations for good dispersion.

The observed shift in the IEP as a consequence of dispersant addition was found to be consistent with the electrical double layer model of surfactant adsorption.

The estimated specific energies of interaction for the powder-polyelectrolyte combinations studied as part of this investigation were in the range of 8–9 Kcal/mole, indicating strong affinity between the polyelectrolyte and the ceramic surfaces.

Acknowledgements

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Electronic mechanism of sintering: Some case studies on real systems

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Abstract. The paper reviews the role of electronic configuration model of condensed state in explaining the sintering behaviour of various alloys. The systems are copper base alloys, ferrous alloys containing phosphorus, tungsten based heavy alloys, Al-refractory carbide composites, 6061 Al-alloy composites, high speed steel composites and tungsten carbide based cemented carbides. These studies cover the research activities of the Powder Metallurgy Laboratory at IIT, Kanpur.

Keywords. Sintering; powder metallurgy; electronic mechanism; sintered alloys; sintered particulate composites.

1. Introduction

Among the numerous attempts in interpreting the sintering mechanisms—reactions at the surface and particle boundaries, surface and volume diffusion and thermally activated dislocation processes are more prevalent. Considerable disagreement exists on the sintering mechanisms operative at different stages. Kuczynski (1949) propounded the diffusion mechanism, while Lenel (1966) used the concept of dislocation mechanism of deformation. In general, the concepts of diffusion theory, creep and recrystallization (Frenkel 1946; Pines 1954; Fedorchenko *et al* 1970) have been mainly used, each of which correctly reflects one or the other group of sintering phenomena. However the construction of these theories on an atomic level limits their possibilities and does not allow a single sintering theory, for which it is essential to consider these phenomenon on a subatomic electronic level (Samsonov 1967).

At present, a number of models of the condensed state of matter have been developed, including the model of configuration localization (Samsonov 1968; Samsonov *et al* 1971), which can be successfully applied in interpreting powder metallurgical processes. The essence of this model is that the valence electrons of isolated atoms are divided into localized and nonlocalized (collective) parts. The localized part forms configurations which are responsible for a minimum store of free energy. Such configurations are s^2 for s -elements, d^0 , d^5 , d^{10} , f^0 , f^7 , f^{14} for transition metals and sp^3 and s^2p^6 for the sp -elements. The energetic stability of the s - and sp -configuration decreases while that of the d - and f -configurations increases with increase in the principal quantum number of the valence electrons. The electronic exchanges between stable and nonlocalized configurations is responsible for the attractive force between the atom cores, whereas electron-electron interaction between nonlocalized electrons is responsible for the repulsive force.

Assuming that for transition metal atoms in the free state with the number of

d -electrons $n_d \leq 5$, only two stable configurations d^0 and d^5 of localized electrons are formed, the statistical weight of atoms having stable configuration (SWASC), d^5 in the metallic crystal was reported (table 1). Similarly for metals with $5 \leq n_d \leq 10$, the SWASC of d^5 and d^{10} configurations were reported (table 1).

The correlation of self diffusivity data with electronic configuration has been done by Upadhyaya (1971c) elsewhere.

Numerous examples of the interpretation of diffusion parameter in heterogeneous systems have also been reported (Upadhyaya 1971a). They show that the electronic concept fully describes the process, irrespective of the fact to which class of electronic analog the partners of the system belong. Similarly it has been noticed that the activation energy for recrystallization of transition metals is a direct function of the degree of localization of the d^5 configurations. In case of refractory compounds based on early transition metals too a similar pattern is observed (Samsonov and Boschko 1970). A detailed review on electronic mechanism of powder metallurgical processing of high temperature material has been done by Samsonov and Upadhyaya (1972).

A common objective of sintering studies is the achievement of an understanding of the effect of sintering variables—temperature, time, applied pressure (if used), powder size, and composition (including additives and atmosphere control—so that

Table 1. Statistical weight of stable electronic configurations of transition metals.

Metal	Electron configuration	SWASC (%)		
		d^0	d^5	d^{10}
Sc	$3d^1 4s^2$	84	16	0
Ti	$3d^2 4s^2$	57	43	0
V	$3d^3 4s^2$	37	63	0
Cr	$3d^5 4s^1$	27	73	0
Fe	$3d^6 4s^2$	0	54	46
Co	$3d^7 4s^2$	0	28	72
Ni	$3d^8 4s^2$	0	12	88
Cu	$3d^{10} 4s^1$	0	8	92
Y	$3d^1 5s^2$	73	27	0
Zr	$4d^2 5s^2$	48	52	0
Nb	$4d^4 5s^1$	24	76	0
Mo	$4d^5 5s^1$	12	88	0
Ru	$4d^7 5s^1$	0	80	20
Rh	$4d^8 5s^1$	0	60	40
Pd	$4d^{10} 5s^0$	0	18	82
Ag	$4d^{10} 5s^1$	0	4	96
La	$5d^1 6s^2$	70	30	0
Hf	$5d^2 6s^2$	45	55	0
Ta	$5d^3 6s^2$	19	81	0
W	$5d^4 6s^2$	0	96	4
Re	$5d^5 6s^2$	0	94	6
Os	$5d^6 6s^2$	0	84	16
Ir	$5d^7 6s^2$	0	68	32
Pt	$5d^9 6s^1$	0	40	60
Au	$5d^{10} 6s^1$	0	10	90

suitable control of variables can lead to products with the required microstructure (commonly small grain size) and high density.

One major difficulty in understanding the exact means of operation of an additive is that so many alternative mechanisms for these processes exist. Thus for example the additive can work as a second phase or as a solid solution. As a second phase (i) providing a continuous high diffusivity pathway e.g. liquid phase at the boundaries, and (ii) providing a continuous low diffusivity pathway at the boundaries for diffusion across the boundary which then acts to restrain grain boundary movement and as a solid solution (i) enhancing diffusion coefficients for the controlling species in the lattice or parallel to the grain boundary by effecting the point defect concentrations in the boundary or lattice, (ii) slowing grain boundary movement by forming a segregated layer at the boundary which must then be pulled along by the boundary, (iii) altering the overall driving force for sintering by altering the ratio of grain boundary energy to free surface energy and (iv) slowing intrinsic grain boundary movement by reducing the diffusion coefficient for atom movement across the grain boundary, again by affecting the defect chemistry.

2. Sintering and phase diagram

Activated sintering allows for either a lower sintering temperature, a shorter sintering time, or improvement in properties from a chemical addition to the powder. One of the most dramatic examples of activated sintering occurs when tungsten or molybdenum is treated with certain transition metals (German and Munir 1982; Petzow *et al* 1982). Figure 1 shows an ideal phase diagram for activated sintering systems (German and Robin 1985). The factors are solubility, segregation and diffusion, as described here: (i) solubility: The additive must have a solubility in the base metal in order to exhibit a favourable effect on diffusion, (ii) segregation: during sintering, the additive must remain segregated at the interparticle interfaces to remain effective during the entire sintering cycle and (iii) diffusion: $D_E \gg D_B$, where D_E is the diffusivity of the base metal B in the additive layer, and D_B is the self diffusivity of the base metal B.

In two-phase systems involving mixed powders, liquid formation is possible because of different melting ranges for the components. In such a system, the

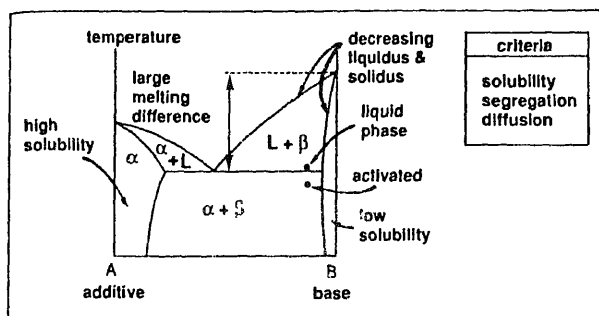


Figure 1. An idealized binary phase diagram for an additive A that acts to enhance the

liquid may provide for rapid transport and therefore rapid sintering if certain criteria are met (Lenel 1980; German 1985; German and Robin 1985). These criteria are similar to those for activated sintering. The liquid must form a film surrounding the solid phase. Thus, wetting is the first requirement. Secondly, the liquid must have a solubility for the solid. Finally, the diffusive transport for the solid atoms dissolved in the liquid should be high enough to ensure rapid sintering. The formation of a liquid film provides the benefit of a surface tension force acting to aid densification and pore elimination. The correlation of such physical properties with the electronic structure has been done by Upadhyaya (1971b) elaborately. The relationships of the phase diagrams with electronic structure is also reported elsewhere (Samsonov and Upadhyaya 1969).

Upadhyaya and Bhattacharjee (1991) investigated the liquid phase sintering response of Cu base alloys containing various additives like Ag, Si, Sn and Pb, such that the liquid phase was 5 mass%. The sintering temperatures selected were 1.1 and 1.2 times greater, respectively than the corresponding isotherms in the binary phase diagrams. Results (figure 2) showed that the highest densification parameter among all the alloys considered was found in Cu-Si alloy. It is worth noting that Cu-Si forms a series of intermetallics whereas Cu-Ag do not form any intermetallics. It is thus evident that in the former the sintering is more enhanced due to the better possibilities of segregation effect. As Si is a covalent bonding

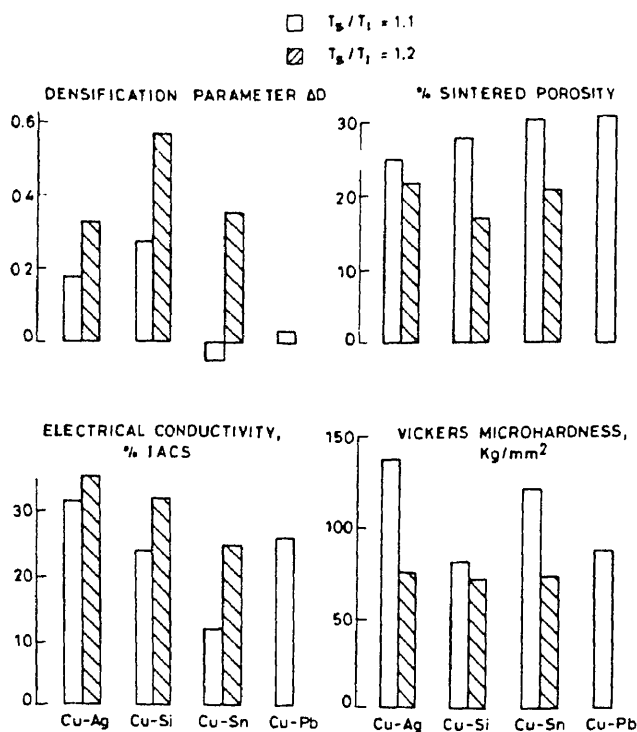


Figure 2. Sintered properties of Cu base alloys liquid phase sintered at two-temperature (T_s and T_l are the sintering and isotherm temperature respectively in degrees Kelvin) (Upadhyaya and Bhattacharjee 1991).

additive, there is more directional bond, thus occupying more space, which in turn would demonstrate higher densification during sintering.

Another interesting example of the German model is in explaining the enhanced sintering of tungsten or molybdenum containing nickel as additive (figure 3).

3. Specific case studies

In the following sections the various findings on sintering studies on binary and multicomponent systems carried out at the Indian Institute of Technology, Kanpur have been briefly described and their interrelationships with the electronic structures have been highlighted.

3.1 Copper based alloys

The sintering results by Upadhyaya and Singhal (1979) on Cu-7Al premix containing transition metals (0–3 mass%) after 950°C sintering revealed that such additions imparted growth to the compacts in the descending order Co-Mo-Fe-Ni (figure 4). The very promising influence of nickel among all the transition metal additions in aluminium bronze has been justified by Mitani and Yokota (1975) who showed the suppressing of Kirkendall effect after nickel addition, thus lowering growth.

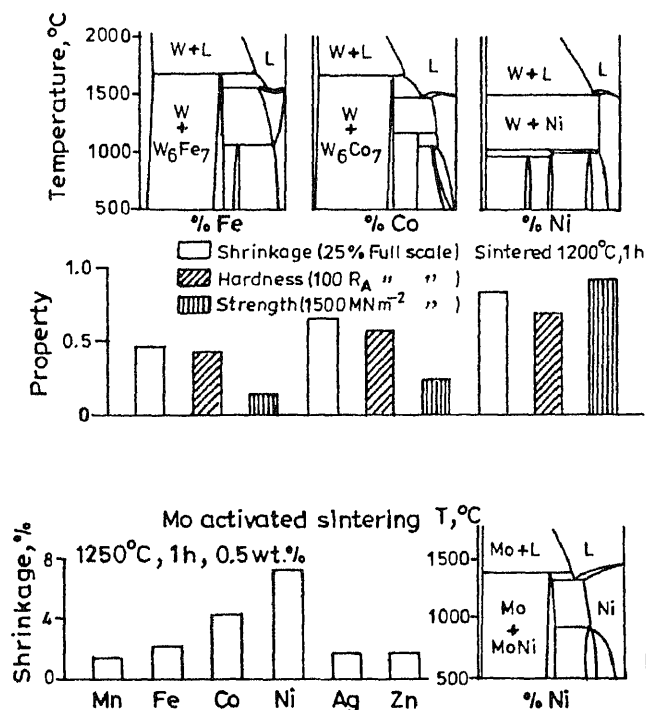


Figure 3. Comparison of phase diagrams and sintered properties for tungsten and molybdenum containing 0.5 mass% transition metal additives (Rabin and German 1985).

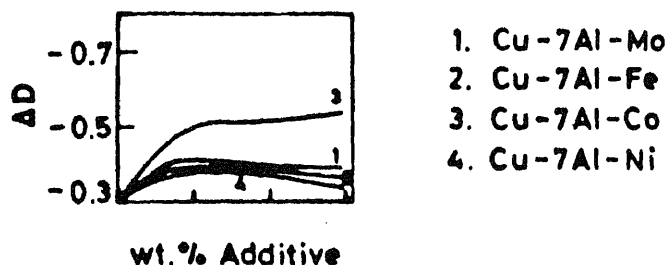


Figure 4. Sintering behaviour of Cu-7Al alloy containing transition metal additives (Upadhyaya and Singhal 1979).

For activated sintering to occur, one needs higher diffusivity, which in other words means higher contribution of nonlocalized valence electrons or lower SWASC values. This is the reason why molybdenum and cobalt having higher SWASC d^5 and d^{10} , respectively show relatively poor sinterability. However a question still remains unsolved as to why nickel with higher d^{10} SWASC than iron and cobalt still shows opposite behaviour. This could be explained on the basis of Haworth and Hume-Rothery (1952) concept that with dissolution of nickel in copper or Cu-Al, the normal tendency to fill the d -shells is counteracted by the effect of the greater freedom of nickel atoms.

Diffusion data (Butrymowicz *et al* 1977) suggest that activation energy of interdiffusion of copper rich side of Cu-Ni alloy decreases with increase in nickel concentration. Such a behaviour would naturally enhance densification due to increased diffusivity. A question remains unanswered as to why cobalt containing bronze also shows a similar pattern with increase in cobalt content, although the activation energy pattern is other way round. This may be correlated with the possibility of increase in SWASC d^{10} in cobalt with increase in temperature, a feature more pronounced in cobalt, which has lower SWASC d^{10} than nickel at ordinary temperature.

A detailed investigation on sintering of prealloyed Cu-35.6 Zn brass powder with transition metal additives like molybdenum, iron, cobalt and nickel (up to 3 mass%) was carried out by Srivastava and Upadhyaya (1985). Sintering temperatures were 700, 800 and 850°C, the atmosphere being dry hydrogen. The densification behaviours with iron or cobalt additions were similar, being superior to those with molybdenum or nickel addition (figure 5). This suggests that the metals with highest d^5 or d^{10} configurations exhibit indifferent behaviour, while those with intermediate range of d^5 configurations i.e. iron and cobalt, have better probability of interaction and thus impart densification.

3.2 Fe-P-X (X = Mo, Ni, Cu) alloys

Hamiuddin and Upadhyaya (1979, 1980a, b) did extensive investigation on the liquid phase sintering of Fe-P-X systems, and found that Mo addition imparted maximum densification among all (figure 6). Next to this came nickel and finally copper, which have energetic stability in the descending order. It is noteworthy that copper

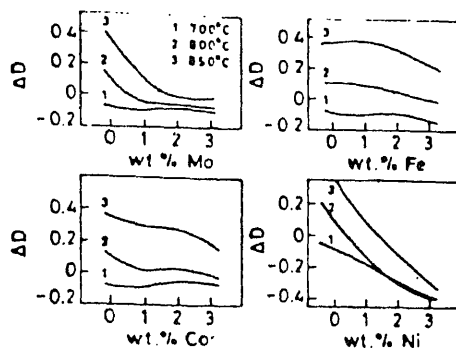


Figure 5. Sintering behaviour of brass containing transition metal additives (Srivastava and Upadhyaya 1985).

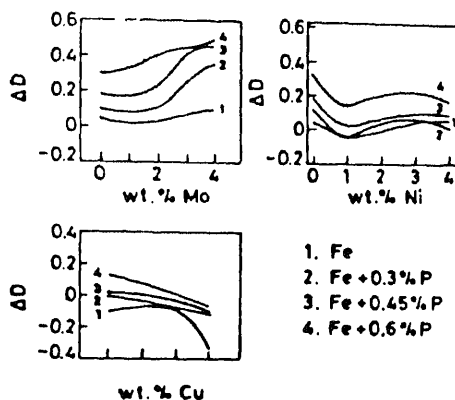


Figure 6. Sintering behaviour of Fe-P premixes containing transition metal additives (Hamiuddin and Upadhyaya 1979, 1980a, b).

having filled d^{10} electrons tries to maintain its own environment during alloying, thus imparting growth. As far as nickel is concerned, which has two $3d$ -electron vacancies, one needs a greater proportion of its addition in iron for densification. In other words, in lower nickel concentration the densification behaviour of iron is an extension of what is observed in Fe-Cu alloys i.e. growth.

3.3 Tungsten based heavy alloys

Srikanth and Upadhyaya (1985a, b) and Upadhyaya and Srikanth (1985a, b) studied the sintering of 90W-10 (X, Ni) heavy alloy system with varying proportions of X (Cu, Fe, Co or Cr) from 0-100%. The results established that after sintering at 1500°C for 1 h densification increased in the sequence Cr-Cu-Fe-Co-Ni (figure 7). A cursory look on the solubility relationship of tungsten in the binder metals reveals that the maximum solubility falls in the sequence Ni (40%) -Co (35%) -Fe

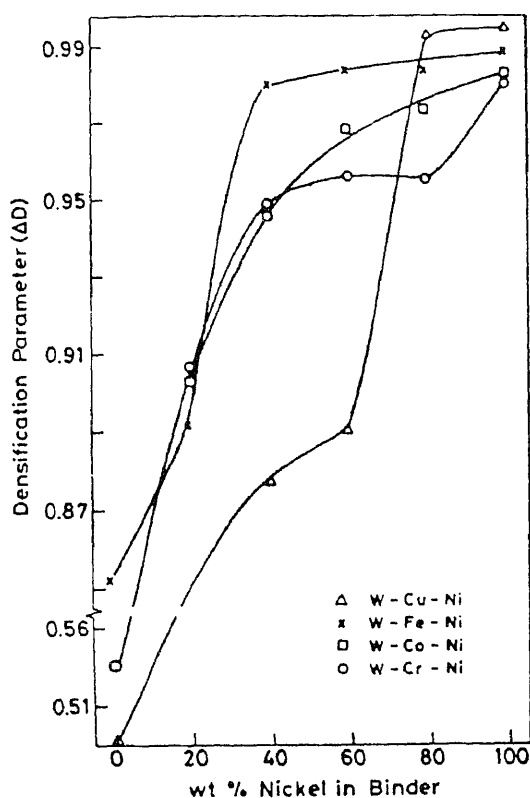


Figure 7. Sintering behaviour of various tungsten based heavy alloys (Srikanth and Upadhyaya 1985a, b).

(33%) -Cu (0%). The W-Cr binary phase diagram is entirely different from the others in the sense that it forms isomorphous solid solution at elevated temperatures with some miscibility gap. This is the reason why all the results on W-Cr-Ni heavy alloys presented by the author do not follow a clear cut correlation. As the difference in d^5 statistical weight between tungsten and chromium is not very large; they form isomorphous solid solutions. On the other hand a very large difference in statistical weight as in the case of W-Cu (88%) results in practically no interaction, whereas the situation for other transition metal binaries are intermediate ones.

3.4 Al-refractory carbide composites

Aluminium refractory carbides are a unique combination in which both aluminium and carbon belong to sp electronic configuration. Upadhyaya and Misra (1978) studied such composites with carbides like TiC, ZrC, Cr_3C_2 , NbC, Mo_2C and WC. TiC addition gave highest densification, while Cr_3C_2 the least (figure 8). As it is well known, TiC, because of its highest degree of SWASC sp^3 , has the highest hardness among all the carbides, which would promote residual stresses at the metal matrix interface and thus activate the sintering process. The poor response

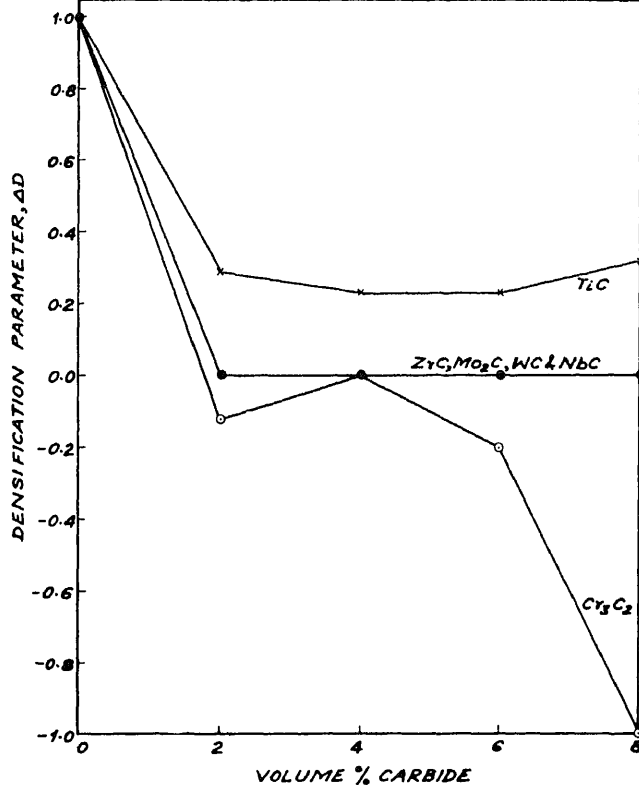


Figure 8. Densification behaviour of Al-carbide sintered composites (Upadhyaya and Misra 1978).

by Cr_3C_2 having lower SWASC sp^3 is also due to its complex crystal structure (rhombohedral), which incorporates a higher degree of anisotropy in the system. While considering the stable configuration formation, the question arises which of the two sp type element C or Al will have the higher energetic stability for sp^3 configuration. The answer is carbon, as it has lower principal quantum number in comparison to aluminium. A more conclusive picture can be drawn, when it is assumed that nonlocalized electrons strongly form hybrid states with both d^n and $s^x p^y$ states.

3.5 The 6061 Al-alloy based composites

The 6061 aluminium alloys contain silicon and magnesium to render them heat treatable. If one looks at the relevant binary phase diagrams, it is apparent that the difference in the melting point of base metal aluminium and the eutectic isotherm of Al-Mg (211°C) is greater than that for Al-Si (86°C). Further, the solubility of magnesium in aluminium is 12 mass%, whereas the solubility of the other constituent namely silicon is practically nil. This clearly indicates that the presence of magnesium in 6061 alloy has a pivotal role during sintering. From the

aluminium as compared to silicon in aluminium is a direct manifestation of this fact. Jha *et al* (1988, 1990) extensively studied sintering of 6061 Al-alloy based composites containing soft (graphite and talc) and hard (alumina and TiC) particles. Apart from the physical modelling of densification, the role of chemical bonds within the dispersoid and at matrix/dispersoid interfaces is also important. Both graphite and talc have weak Vander Waal type forces between the layered structures, whereas, alumina and TiC are covalently or covalent/ionic bonded. The sintered porosity variation of 6061 base composite (figure 9) amply illustrates the above fact such that graphite/talc addition increases porosity level, whereas, TiC and alumina addition exhibit reverse trend.

3.6 High speed steel composites

High speed steels (HSS) are a range of highly alloyed steels which offer high hot hardness, wear resistance and toughness. These properties are best achieved by an alloy consisting of uniform dispersion of fine, hard, stable particles such as carbides in a tough matrix. Supersolidus liquid phase sintering of high speed steels is a standard economical practice, which avoids carbide segregation and grain growth. Kar and Upadhyaya (1990, 1991) and Upadhyaya and Kar (1992, 1993) extensively studied the role of TiC and TiN additives up to 8 Vol. % on sintering behaviour of T15 (Cr 4.23, Co 4.99, Mo 0.55, W 12.50, V 4.75, C 1.59%) and T42 (Cr 3.96, Co 10.60, Mo 4.01, W 9.70, V 2.39 and C 1.38%) grades of high speed steels.

From the literature survey it emerges that all the refractory compound enriched HSS compositions can be classified into three groups. The first group of compounds, which dissolve completely in the matrix at the sintering temperature, do not serve

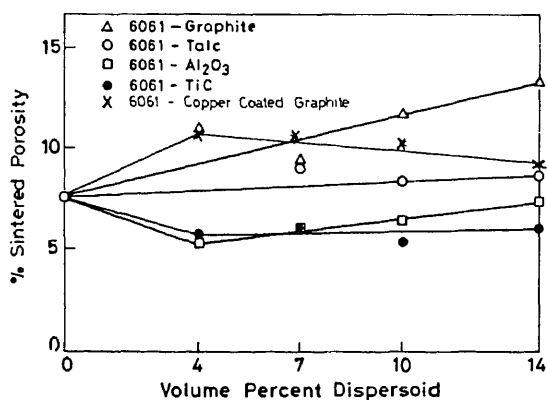


Figure 9. Variation of porosity of argon sintered 6061 alloy based composites as a function of dispersoid content (Jha and Upadhyaya 1988).

carbide and chromium carbide in steels. The second group of compounds are refractory carbides such as WC, Mo₂C and VC etc. which are inherent in the microstructure of the steels. Their evolution can be brought about by a change in the chemistry and heat treatment of the steel. The presence of such compounds does not change the sintering conditions as wettability and bonding in the matrix do not pose any problem. The third group of refractory compounds are those which remain stable in the matrix at still high temperatures. TiC and TiN fall in this group of the refractory compounds. The relative advantage of their addition depends on the wetting characteristics and so the bonding between the hard particles and matrix. TiC has better wetting behaviour (contact angle < 90°) as compared to TiN (contact angle > 90°) with iron. Better densification behaviour in case of TiC containing composites based on either T15 or T42 HSS in comparison to those containing TiN (figure 10) is related to the higher wettability of TiC as compared to TiN. For either of the selected refractory compound, it is obvious that composites based on T42 HSS have better densification behaviour in comparison to the corresponding T15 HSS based composites. This difference in the densification behaviour is attributed to molybdenum and relatively higher cobalt content in T42 HSS than that in T15 HSS.

The distinctive densification response in either TiC or TiN containing composites

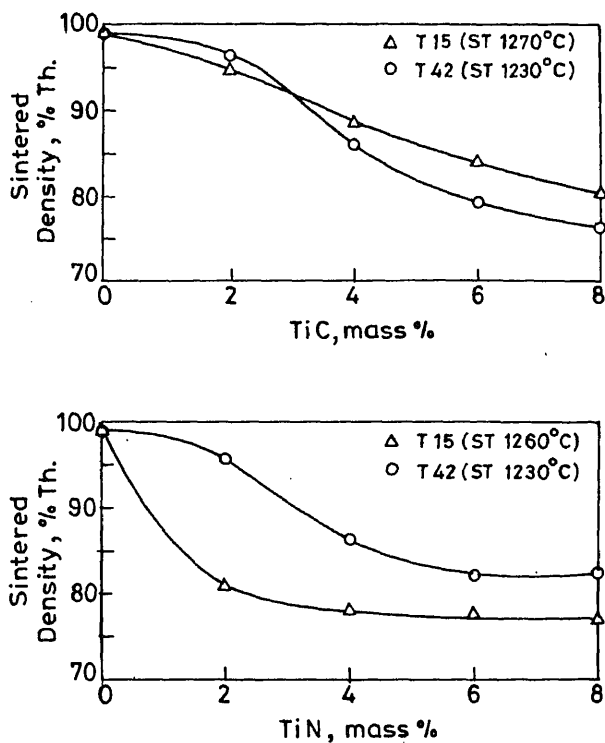


Figure 10. Effect of TiC and TiN additions on the densification of T15 and T42 grade high speed steels after supersolidus liquid phase sintering (Upadhyaya and Kar 1992, 1993).

can be adequately correlated on the basis of the differences in bondings, which these compounds possess. Titanium in refractory compounds e.g. TiC/TiN, pertains to early transition metal containing unfilled d shell, while both carbon and nitrogen correspond to sp electronic configuration for their valency electrons. Samsonov (1980) discussed in detail the energetic stability of both types of elements and concluded that during formation of such refractory compounds the transition metals act as donors of electrons, so as to stabilize the sp^3 configuration of non metal atoms to different extents. Carbon whose isolated atoms possess s^2p^2 electronic configuration tend to acquire stable sp^3 configuration due to $s-p$ transition during TC formation. However, in case of nitrogen, whose isolated atoms have s^2p^3 configuration, owing to $s-p$ transitions by the scheme $sp^4sp^3 + p$, they fully tend to acquire sp configurations with one weakly bonded electron of p configuration. This third extra unbonded electron which is responsible for relatively lower hardness, lower melting point and higher plasticity in TiN as compared to strongly covalent bonded TiC. The poor wettability of TiN with HSS melt is a direct manifestation of the above fact. Moreover, the enhanced matrix grain coarsening in case of TiN containing composites in a way is also related with the above findings, since in order to attain pure full density a relatively higher sintering temperature was necessary.

WC based cemented carbides

Upadhyaya and Basu (1985) reported sintering results on WC-10 Co hard metals, where the cobalt binder was partially or fully substituted by other transition metals like iron and nickel. For an efficient liquid phase sintering, wettability of melt is an essential criterion. WC has excellent wettability with iron-group transition metals, as compared to IV and V group transition metal carbides. This has been explained by Upadhyaya (1984) on the basis of chemical bonding in the respective refractory carbides. The solubility of carbide phase in the binder melt can also be explained on the basis of above reasonings. Among all the binders studied by author, WC-Fe and WC-Co form pseudobinary systems whereas WC-Ni does not. The almost filled d configuration of nickel, brings forth the obvious conclusion as to why WC-Ni hard metal is not an ideal one. Solubility data confirm that cobalt (MP 1495°C) dissolves 10-22% of WC at the eutectic temperature of 1320°C, whereas iron (MP 1535°C) dissolves a lower quantity (7.5%) at the corresponding eutectic temperature (1143°C). The results show that iron may be an efficient binder candidate provided WC solubility range in it could be increased. Although the solubility of WC in nickel is not small, the exploitation of the system could not be made as they do not fall in an equilibrium pseudobinary system.

The continued increase in the consumption of WC based cemented carbides and the threat from the depleting resources of tungsten and cobalt have attracted a lot of attention so as to develop alternate composition compatible with WC-Co based ones. The most reasonable approach seems to dilute WC by other refractory carbides and partial replacement of the cobalt binder by nickel, iron or their alloys. Bhaumik *et al.* (1992a, b, 1994) extensively studied the sintering behaviour of WC-10 Co corresponding to 17 Vol. % binder phase. All the subsequent compositions developed were tailored so that the volume fraction of hard and binder phases remained constant as that of the initial WC-10Co cemented carbide. The hard phase WC was replaced by TiC, Ti(CN) or TiN about one third by volume. The partial

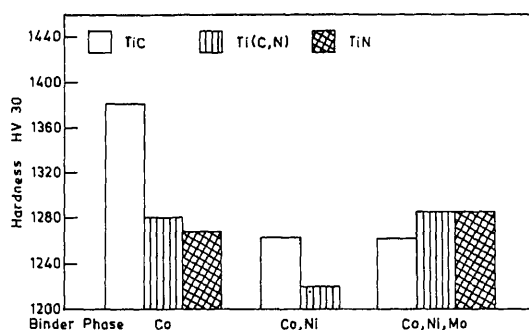


Figure 11. Hardness variation of WC-10 Co based cemented carbides as a function of binder phase substitution (Bhaumik *et al* 1992a, b, 1994).

substitution of cobalt (50%) by nickel in binder necessitated the introduction of Mo_2C for better wettability. In general, it was noticed that the properties of Ti (C, N) containing cemented carbides were intermediate to those containing TiC or TiN irrespective of the change in the binder chemistry. The properties of the former group i.e. those containing Ti (C, N) were however, much closer in magnitude to those containing TiN (figure 11). It is interesting to note that both TiN or Ti (C, N) additions to WC-10 Co cemented carbide gave rise to processing difficulties such that the full density was not achieved during normal pressureless liquid phase sintering. This necessitated the application of another step hot isostatic compaction after the liquid phase sintering. The role of electronic structure of component atoms in the refractory compounds has already been highlighted in §3.5.

4. Conclusions

It follows from the above considerations that consolidation process through sintering can be interpreted on the electronic structure, making it possible to propose a unified theory. To this end, it is essential to concentrate attention on the physico-chemical process of materials during sintering and also as the quantitative development of the model of electronic structure so as to establish a direct relationship between the electronic structure, technological parameters and the end materials properties.

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Equation of state of refractory materials at very high temperatures—theoretical and experimental studies

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Abstract. This paper describes some of the theoretical and experimental studies being carried out at IGCAR on the equation of state of refractory materials like reactor fuels at high temperatures (>3000 K). The equation of state is primarily calculated by the principle of corresponding states. The influence of these equations of state on energy release in a hypothetical core disruptive accident in a fast breeder reactor is indicated. Details of an experimental facility based on laser induced vapourization mass spectrometry, which is being developed to measure the vapour pressures of materials at high temperatures is presented. Possible applications of this facility in other fields of materials research are indicated.

Keywords. Equation of state; laser induced vapourization; mass spectrometry; refractory materials; nuclear fuels.

1. Introduction

Modern technology demands high temperature and high performance materials such as advanced ceramics, composites and other refractory materials for a variety of applications in space technology (vehicle reentry, missiles etc.), fusion research (first wall material in fusion reactors) and nuclear reactors. These materials often get exposed to very high temperatures (>2500 K) in advanced material processing technologies such as chemical and physical vapour deposition, plasma and laser processing and surface modifications. In order to understand the behaviour of these refractory materials at very high temperatures, it is necessary to establish their equations of state at such elevated temperatures. These properties are especially required to analyse accident conditions.

As an example, let us consider nuclear reactor fuels. Off-normal events in liquid metal cooled fast breeder reactors (LMFBRs) can result in the release of a large amount of energy. Such events have the potential of taking the reactor fuel or a portion of it to very high temperatures (up to 5000 K) and can lead to partial or complete disassembly of the core. This type of an event is only postulated and hence it is called hypothetical core disruptive accident (HCDA). The analysis of this type of accident requires a knowledge of the equation of state (EOS) of the reactor fuel at high temperatures (IAEA-IWGFR/26 1978). The energy release in such accidents depends strongly on how quickly the vapour pressure develops. The designer has, therefore, to tackle the problem of making accurate estimates of the equation of state of the fuel material. The equation of state for the widely used fuel, namely, UO_2 is fairly well known, though based on limited experimental data (Bober *et al* 1987; Breitung and Reil 1989) and general theoretical models (Fischer 1989). The experimental data on other types of fuels such as carbides, nitrides and metal alloy fuels are not available and theoretical calculations have led only to estimates.

Theoretical approaches to EOS of such refractory materials are based on the principle of corresponding states (PCS) (Browing *et al* 1978) and the significant structure theory (SST) (Eyring and John 1969). Both these models have been applied mostly to organic and simple inorganic systems at temperatures much lower than the region of our interest. They yield parametrized equations whose parameters are obtained by fitting the equations to experimental data. In the case of refractory materials, experimental data are not available at high temperatures. Hence experimental and theoretical studies have to go hand in hand.

Conventional experimental techniques which are used for the measurement of thermophysical properties of refractory materials below 2500 K cannot be used at ultra high temperatures (> 3000 K) because of obvious limitations such as: (i) non-availability of inert container material at such elevated temperatures, (ii) difficulty in attaining and controlling such high temperatures and (iii) difficulty in the measurement of physical and chemical properties under these conditions. For example, the Knudsen effusion technique is often used to measure vapour pressures of refractory materials at low temperatures (< 2500 K). However, this demands that the pressures be in the Knudsen effusion collision-free regime (10^{-4} atm). Under these conditions it is possible to determine the composition of the vapour phase of the system without difficulty. But at high temperatures, the pressures will be much higher, of the order of an atmosphere or higher. Apart from the difficulty of sustaining solid-vapour equilibrium under such high temperature, high pressure conditions, pressure measurement corresponding to the equilibrium temperature and gas sampling are difficult problems. One way of avoiding these problems is by using a dynamic pulse heating technique so that (a) the sample itself acts as a container (therefore no container problem), (b) temperature is generated for a very short duration (order of millisecond or less), limiting energy requirements, and (c) heating is done on a very small sample area and local thermodynamic equilibrium is established at that point during the short duration of heating.

Four different methods of pulse heating, namely, exploding wire technique, electron and neutron pulse heating and laser heating have been employed for this purpose (Ohse *et al* 1980). Of these, dynamic laser pulse surface heating technique is adopted and developed here—because this method provides a better access to the analysis of the gaseous molecules that are formed during the laser heating of the sample—by using mass spectrometric and spectroscopic techniques (Ohse 1985; Hastie *et al* 1988; Olender 1990). This will lead to a better understanding of the equilibrium conditions. Hence we have chosen a high power pulsed laser as the heat source to attain these high temperatures in a container-less fashion and a mass spectrometer to characterize the vapour species in order to generate the EOS of technologically important high temperature refractory materials. For this purpose, we have built a laser-induced vapourization mass spectrometer (LIV-MS) in our laboratory.

In this paper we first present the calculation of the equation of state for different fuels, including that of mixed carbide fuel, $[(U_{0.3}Pu_{0.7})C]$, used in the fast breeder test reactor (FBTR), at Kalpakkam, by using the principle of corresponding states. This data is then applied to the study of energy release in a typical hypothetical core disruptive accident (HCDA) in a modularized LMFBR. These results provide some insight into fuel behaviour under such extreme conditions. We will then discuss the LIV-MS system developed in-house for generating the vapour pressure data of reactor fuels at these high temperatures.

2. Calculation of the equation of state

2.1 Method based on the principle of corresponding states (PCS)

Because of experimental difficulties, the vapour pressure data for reactor fuels are generally reported only in the low temperature range (< 2500 K). In order to extrapolate these data to very high temperatures we require a theoretical model. The principle of corresponding states (PCS) has been used for this purpose. PCS is based on the assumption that the equation of states of all materials can be generalized on the basis of their reduced temperature (T_r), reduced pressure (P_r) and reduced volume (V_r), the reduced properties of the system being obtained by scaling the actual value in terms of critical value. Thus if the pressure, volume and temperature of one mole of the material are denoted by P , V and T respectively, (their values at critical points being P_c , V_c and T_c), then the reduced quantities are defined as $P_r = P/P_c$, $V_r = V/V_c$ and $T_r = T/T_c$. PCS asserts that for all the materials the compressibility factor,

$$Z = PV/RT,$$

is the same function of V_r , T_r and α , where α is the Riedel factor, defined as the slope of the reduced vapour pressure vs temperature curve at the critical point (Browing *et al* 1978). This method presupposes a knowledge of the critical parameters. An algorithm for finding the critical constants are based on four fundamental generalized equations deduced from experimental data of many (> 70) organic compounds as given below (Browing *et al* 1978):

$$1/Z_c = 3.72 + 0.26 (\alpha - n), \quad (1)$$

$$\ln P_{lv} = \ln T_r - 0.0833 (\alpha - 3.75) (36/T_r - 35 - T_r^6 - 42 \ln T_r), \quad (2)$$

$$\rho_l^* = 1 + 0.85 (1 - T_r) + (1.93 + 0.2 (\alpha - n)) (1 - T_r)^{1/3}, \quad (3)$$

$$1/2 (\rho_l + \rho_v) = CT + D \text{ (law of rectilinear diameter)}, \quad (4)$$

where Z_c is the $P_c V_c / RT_c$, critical compressibility factor, $\rho_r = \rho / \rho_c$ the reduced density, P_{lv} the reduced saturated vapour pressure and n , a free parameter obtained from experimental data and for organic fluids it was found to have a value of 7. Subscripts c, v, l and r refer to critical point, vapour, liquid and reduced state respectively. C and D are constants of the law of rectilinear diameter used for the calculation of V_c (using estimated T_c and density at melting point).

The estimation of critical constants, P_c , V_c , T_c and α , uses (1)–(4) and requires an iterative algorithm for solving these equations for all the critical parameters and α . The vapour pressure can be obtained from (2). The details can be found in Browning *et al* (1978). The input data required are the melting point (T_m), density at the melting point (ρ_m), volume expansion coefficient (α_m) and vapour pressure at the melting point (P_m).

The validity of these equations when applied to inorganic liquids has not been established experimentally. In order to ascertain the validity of the PCS method to reactor fuels, we tested it on UO_2 which is a relatively well studied system

reported in the literature (Browning *et al* 1978) is indicated in figure 1 as PCS1. We can see that the data obtained do not agree well with the experimental values. Hence the value of n was adjusted to match with the available experimental data on the UO_2 system and that of liquid alkali metals. When the value of n is changed from 7 (PCS1) to 0.7 (PCS2), the results obtained are in reasonably good agreement with the experimental data (Bober *et al* 1987), as well as recent in-pile measurements (Breitung and Reil 1989) and calculations based on significant structure theory (Fischer 1989) as can be seen in figure 1.

Even though UO_2 is being used widely as a nuclear fuel, a mixed oxide of uranium and plutonium is the fuel of choice in most fast breeder reactors. There is considerable interest in newer types of fuels such as carbides, nitrides and metal alloys of uranium and plutonium on account of their superior properties such as higher density, better thermal conductivity and favourable neutronic properties. In

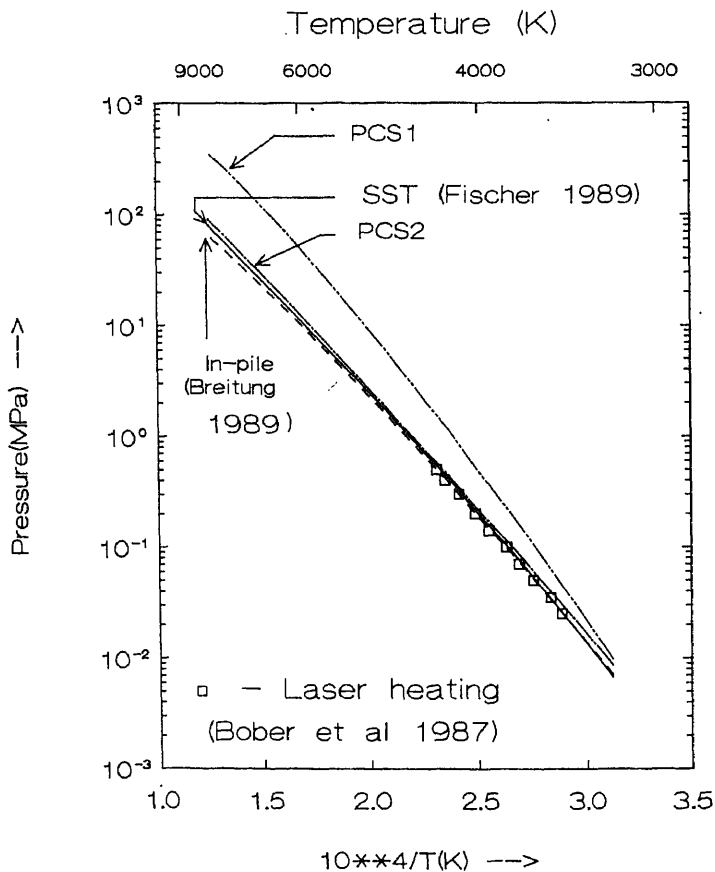


Figure 1. Comparison of vapour pressure of UO_2 in the liquid region by different methods.

fact, the FBTR at Kalpakkam employs a mixed carbide fuel. Hence, the above model (PCS2) was applied to all possible fuel types, namely UC, UO_2 , mixed carbide $[(\text{U}_{0.3}\text{Pu}_{0.7})\text{C}]$, metal alloy $[(\text{U}_{0.6}\text{Pu}_{0.17}\text{Zr}_{0.23})]$, UN, mixed nitride $[(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}]$ and PuN. Wherever experimental data were not available at the required melting point, reasonable estimates were made by employing strategies like extrapolation of low temperature data in order to arrive at the input parameters. The input parameters used in the computation are shown in table 1. The accuracy of the computed equations of state is limited by the input data. Nevertheless, the results bring out trends which are useful in making some broad conclusions. The vapour pressures of different fuels of interest in reactor calculations, in the temperature range from 3000 K to 6000 K, are plotted in figure 2. It is seen that UC has the lowest vapour pressure while PuN has the highest (for $T > 4000$ K). It must be mentioned here that UN and PuN are not reactor fuels, but only fuel materials. The mixed nitride which is a potential fuel, has lower vapour pressure than UN and PuN. Some vapour pressure curves cross each other indicating that even if one system has relatively higher pressure at low temperatures, the trend can reverse at high temperatures. The values of critical constants obtained are shown in table 2. A sensitivity study on the input data showed that the volume expansion coefficient is the most sensitive input parameter (Joseph *et al* 1989).

2.2 Extrapolation method

No experimental data is available on the mixed carbide fuel of the composition that is being used in FBTR (Ganguly *et al* 1988). The low temperature (below melting point) vapour pressure data, for the vapour species Pu(g) , U(g) , $\text{UC}_2(\text{g})$, $\text{C}_1(\text{g})$, $\text{C}_2(\text{g})$, $\text{C}_3(\text{g})$ and $\text{C}_4(\text{g})$ have been computed in our laboratory by thermodynamic modeling (Joseph *et al* 1989). The pressure-temperature data thus obtained is valid only up to temperatures less than the melting point of the carbide and hence this has to be extrapolated across the melting point to temperatures upto 5000 K. A simple and reasonable approach to this extrapolation is to correct the slope of the partial pressure curve of each species for the heat of fusion. Such extrapolation was found to give good agreement with the literature data as well as with the modified PCS, as discussed above, for UO_2 (up to 5000 K). Similarly, good agreement is seen in the case of UC as well (see figure 3). But for the FBTR fuel the agreement between the above extrapolation and the modified PCS method is rather poor (see figure 4), differing by an order of magnitude. This is not

Table 1. Input parameters for PCS.

Fuel	T_m (K)	P_m (atm)	ρ_m (g/cc)	$\alpha_m * e^{-6}/K$	
UO_2	3115	5.4E-2	8.74	103	m - melting point
UC	2780	2.8E-5	9.84	78.1	α - vol. exp. coft.
UN	3035	6.0E-1	11.41	68.2	ρ - density
Alloy	1550	1.3E-8	13.75	74.6	
FBTR	2400	1.1E-3	10.0	77.4	
PuN	2993	1.7E-1	10.76	117	
MN	3053	8.8E-2	11.36	68.4	

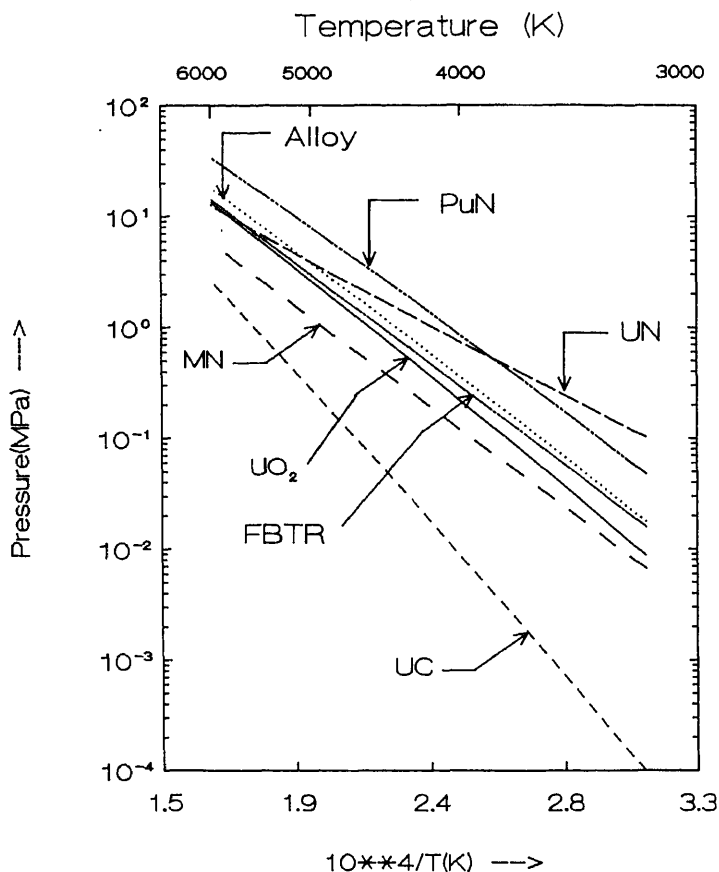


Figure 2. Vapour pressure of different types of reactor fuels in the temperature region of 3000 to 6000 K.

Table 2. Critical parameters for different fuels by PCS.

Fuel	T_c (K)	P_c (atm)	ρ_c (g/cc)	$\log P \text{ (MPa)} = A - B \cdot 4/T + C \log(T)$		
				A	B	C
UO ₂	8098	1017	2.12	11.23	2.478	-1.58
UC	9759	1349	2.24	17.00	3.564	-2.82
UN	10383	2034	2.85	-4.23	1.077	1.89
Alloy	8928	2227	3.09	8.18	2.222	-0.85
FBTR	9221	1403	2.31	5.13	2.050	-0.15
PuN	7329	1227	2.66	10.91	2.24	-1.50
MN	10594	1942	2.75	2.18	1.93	0.48

surprising as the input data is not known very reliably. Extrapolation is from computed partial pressures. As for PCS, input data such as density, volume expansion coefficient and vapour pressure, all at melting point are only estimates. This points to the need for experimental data.

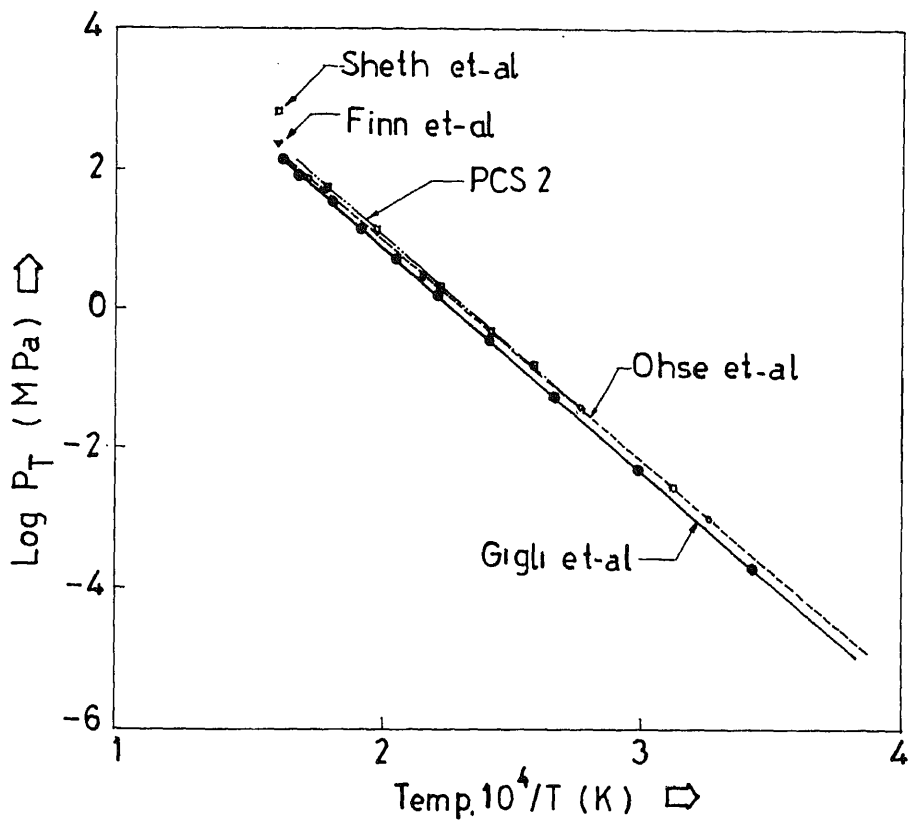


Figure 3. Vapour pressure over uranium monocarbide (3000–9000 K).

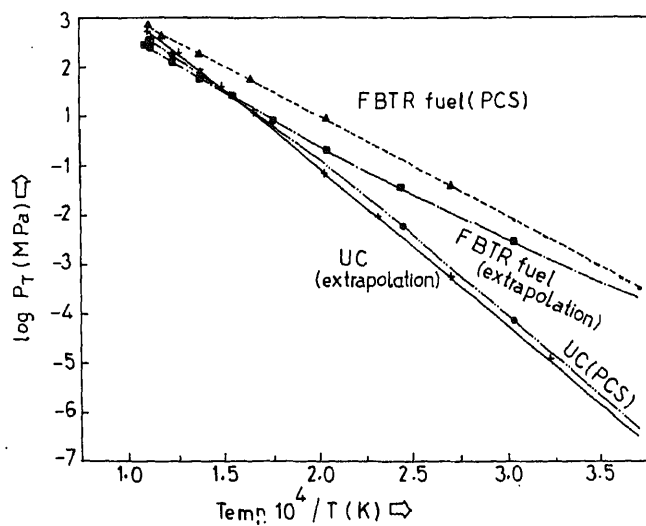


Figure 4. Vapour pressure over uranium monocarbide and mixed carbide (3000–9000 K).

3. Influence of fuel type on the HCDA energetics

The EOS has a strong impact on the magnitude of energy release in an HCDA. In this accident scenario, the power excursion and the energy release are terminated only by core disassembly due to pressure generated on account of the heating of the fuel. Assuming typical initial reactor conditions and those corresponding to a typical unprotected loss of flow accident in a medium sized LMFBR (PFBR-500 being designed in India) for all the fuel types, the core disassembly analysis was performed (Joseph M, Bhaskar Rao P and Mathews C K, to be published) by using the VENUS code (Jackson and Nicholson 1972). The results obtained for the energy release, work potential and peak fuel temperature reached are shown in figure 5. It can be seen that the fuel can reach a peak temperature of around 4500 K and that in that region PuN has the highest vapour pressure and UC the lowest. Correspondingly, the energy release is the highest (6554 MJ thermal and 232 MJ mechanical) in the case of UC and the lowest for PuN (4353 MJ, thermal and 18 MJ, mechanical).

4. Experimental facility for EOS

As indicated above, theoretical tools such as PCS or SST are tested for their validity only for low temperature systems such as organic liquids and simple

TER-Thermal Energy Release(MJ) : PFT-Peak Fuel Temp.(K)

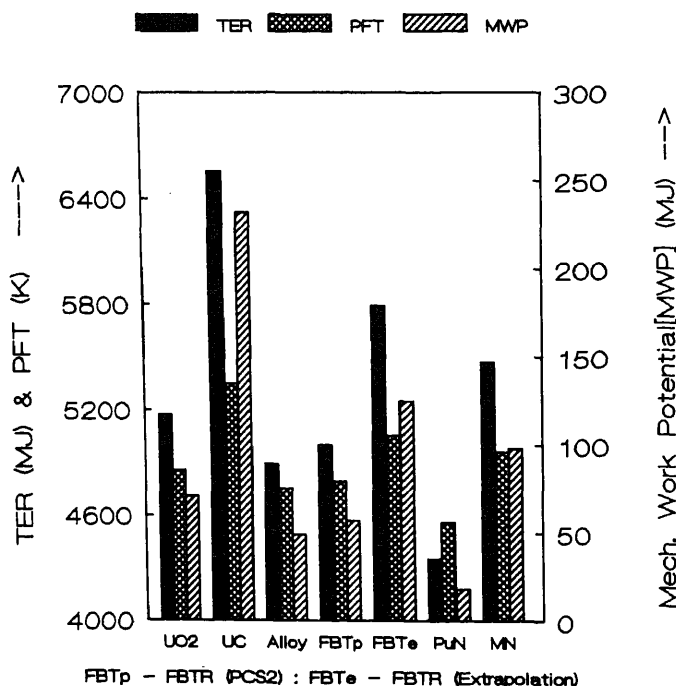


Figure 5. Results of HCDA for different types of fuels.

inorganic materials. They are not tested for refractory materials mainly because of experimental difficulties. We have set up an LIV-MS system to measure the vapour pressure of some of these materials at high temperatures.

The LIV-MS facility primarily consists of a high power pulsed laser which acts as a heat source and a mass spectrometer to characterize the vapour species. A schematic of the experimental facility is shown in figure 6. It is based on three vacuum chambers, of which only two are shown in the figure. The first chamber is pumped by a 2000 l/sec capacity 10 inch, Edwards diffusion pump (model Mk 2/2000). The second chamber is pumped by a 1500 l/sec capacity cryo pump (Leybold AG, Model RW2 compressor) and the third by a turbo pump with a capacity of 1000 l/sec (Leybold, Turbovac 1000 W/L). The three chambers are aligned to have the same axis (that of the molecular beam) by employing a CW He-Ne laser. A skimmer separates the first and second chambers whereas a collimator separates the second and third chambers. Because of the good system conductance, the background pressure is very low ($< 10^{-6}$ torr). Small conductances between the chambers allows for differential pumping. In the first chamber, the vacuum condition permits the establishment of a high gas expansion pressure ratio and there is minimal perturbation of the vapour plume by post-expansion gas collisions with the background gas molecules. (The laser vapourization time is too short, of the order of few μ sec for the ionization gauges to respond).

4.1 The mass spectrometer

The mass analyser used is a quadrupole mass filter (Extrel Corp.) with a mass range of 1 to 700 amu. This is housed in the second chamber such that its axis is perpendicular to the beam path (i.e. crossed beam configuration). The molecular beam coming through the skimmer gets ionized in the ion source of the mass spectrometer. These ions are then accelerated into the quadrupole. The DC and RF voltages of the quadrupole mass filter (QMF) are so adjusted as to allow only

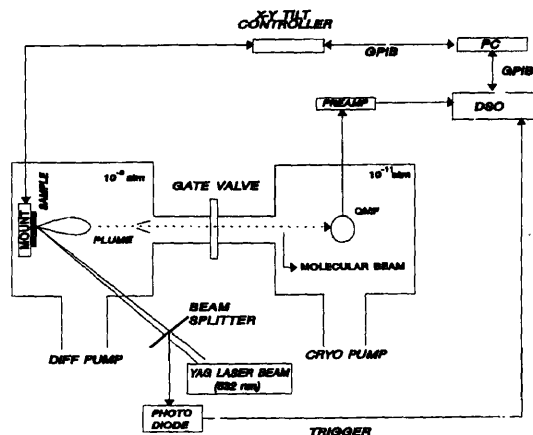


Figure 6. Schematic of LIV-MS facility.

ions of a given m/e to pass through. Mass scan is achieved by varying the DC voltage, while keeping the DC/AC voltage ratio to be constant. The ions are detected by an electron multiplier and the signal is amplified by an analog charge preamplifier. The whole QMF assembly is mounted on an 8 inch UHV flange fixed to one of the side ports of the second chamber.

4.2 The sample positioning system

The sample is placed in the first chamber by mounting it on a kinematic stage (see figure 6). This stage movement is controlled by four DC drive motors, two for axial translation motion and two for tilts in different directions. The range of the translation motion is 25 mm in either direction and tilt is $\pm 7^\circ$ (M/s Physik Instruments, Model C-804). The movement of these motors are controlled remotely through a personal computer (PC). This system allows the sample to be positioned or rastered, as desired, between laser shots. For uniform plume generation, the sample has to be rastered, otherwise a crater of the order of 200–300 μm in diameter will be formed at the laser focusing point and this in turn will decrease the plume intensity. Hence without rastering the sample, we cannot get good reproducibility in ion intensity. A typical raster rate of 100 $\mu\text{m}/\text{sec}$ provides more than 90% shot-to-shot overlap at 10 Hz laser pulsing with a focused spot diameter of $\sim 300 \mu\text{m}$. Figure 7 shows the crater formation on UO_2 pellet for about 1000 laser shots on the same focusing point.

4.3 The laser system

Different types of lasers have been used for the evaporation of refractory materials (Ready 1971; Hastie *et al* 1988; Olender 1990). We have chosen a Nd-YAG laser

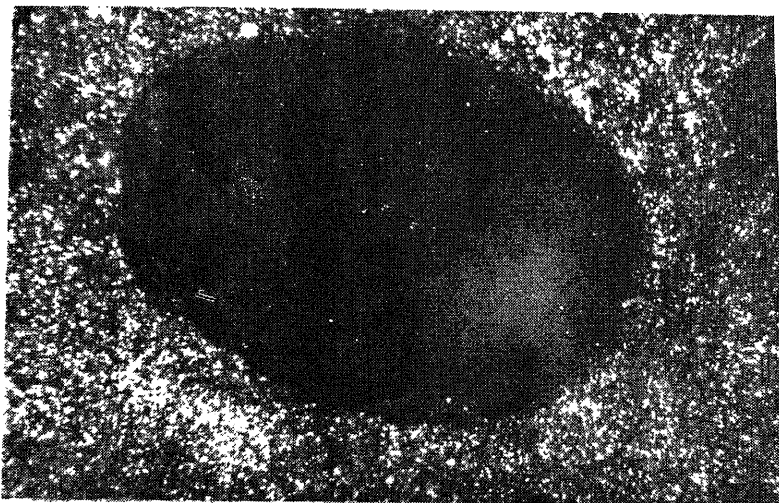


Figure 7. Micrograph of crater formed on UO_2 pellet for about 1000 laser shots. Crater size: about 350 μm dia and 25 μm deep.

system (Continuum, Model NY-61-10) to suit our experimental conditions. The maximum beam energy is 600 mJ at 1064 nm with 5–7 nsec pulse width. The laser is operated in the Q-switched mode at a repetition rate of 10 Hz. The laser beam spatial profile is a Gaussian distribution (TEM_{00}). The laser system is equipped with mixing crystals to provide additional wavelengths at 532 nm (300 mJ), 355 nm (170 mJ) and 266 nm (50 mJ). A laser fluence of 20–40 mJ/cm² at 532 nm was found to be sufficient to generate a reasonably good vapour plume on ceramic materials (Hastie *et al* 1990). In our experiments we have used ~ 50 mJ pulses. The laser beam is directed to the target sample, through a quartz view port, by using suitable dielectric coated mirrors for beam steering and a 250 mm focal length quartz lens for focusing. The power density generated is of the order of 10⁹ W/cm².

4.4 Data acquisition

The ions of interest falling on the detector gives out an analog signal. This signal from the detector is fed to a digital storage oscilloscope (DSO) as indicated in figure 6. In this work we have used a LeCroy model 9450A 300 MHz two channel oscilloscope. This has a 50 K storage memory for each channel with a sampling rate of 400 Ms/S. The laser beam is partially split, before it enters into the vacuum chamber. The less intense of the split beam is made to fall on a photodiode (UT Sensors Inc, Model PIN-HR040). The signal from the photodiode is used to trigger DSO to start the data collection process.

4.5 Measurement

In the actual experiment, the sample position is adjusted to the location of interest and the laser beam is focused. After this the sample is rastered. The plume formed in each laser pulse is skimmed into the second chamber and the molecules in the beam are ionized in the QMF ion source. The mass spectrometer is tuned to the mass of interest (single ion mode), so that the signal is seen on the scope (DSO). In order to get a good signal-to-noise ratio, averaging of the signal is done over 100 to 1000 laser shots. Generally, the collection of the signal for about 5 msec from the start of the laser pulse is found to be sufficient to get the time of arrival (TOA) profile of each ion mass. This 5 msec period includes the time for evaporation of the order of few μ sec, transit of the molecular beam for about 50 cm (the distance from the evaporation surface to the ion source), and electronic detection, including RC time constant. Figure 8 shows a typical mass selected profile of ion intensity for $UO_2(g)$ species. The data collected in the DSO is transferred to a computer for further processing. By tuning the QMF for different masses of interest, the intensity of each species which is formed in the laser evaporation can be obtained.

5. Studies on UO_2 pellet

A UO_2 pellet obtained from the Nuclear Fuel Complex, Hyderabad, was subjected to laser irradiation. The species O, U, UO and UO_2 were identified in the vapour

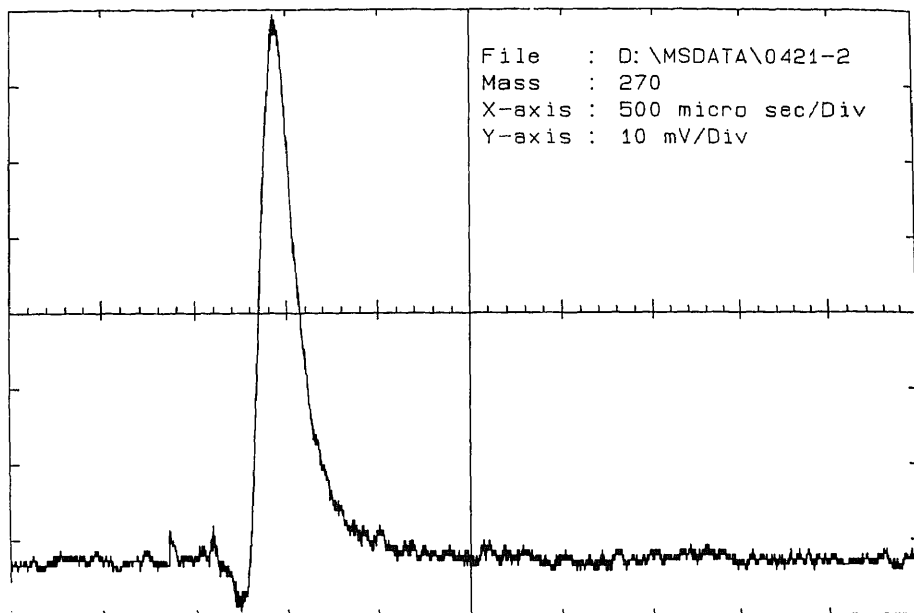


Figure 8. Time of arrival (TOA) profile for $\text{UO}_2(\text{g})$ species

phase by means of the QMF. If these species are in thermal equilibrium with each other, say at temperature T , then according to the kinetic theory of gases,

$$\frac{1}{2} M \bar{v}^2 = \frac{3}{2} KT,$$

i.e.

$$\frac{1}{2} M (\frac{d}{t})^2 = \frac{3}{2} KT,$$

$$t \propto \sqrt{M/T},$$

where, M is molecular weight of the individual species, K the Boltzman constant and t is the time of arrival (TOA) as shown in figure 8. Hence, a plot of the time of arrival as a function of the square root of molecular weight should yield a straight line. Figure 9 shows the plot obtained in the present experiment. The straight line nature of the plot shows that the gas species are in thermal equilibrium with each other, at least with respect to translational energy. The temperature which can be obtained from the slope of the linear plot corresponds to a cool beam, which results from the supersonic expansion of the plume.

In laser evaporation, the plume formation can be considered to be similar to the beam formation process of supersonic expansions through a nozzle, where the beam composition after the expansion will be same as that of the pre-expansion temperature and partial pressure conditions (Bonnell and Hastie 1979). The high pumping speed of the vacuum system and the pulsed nature of vapour evolution process also ensure the production of high expansion ratios, which is a necessary condition for 'freezing in' the species distribution.

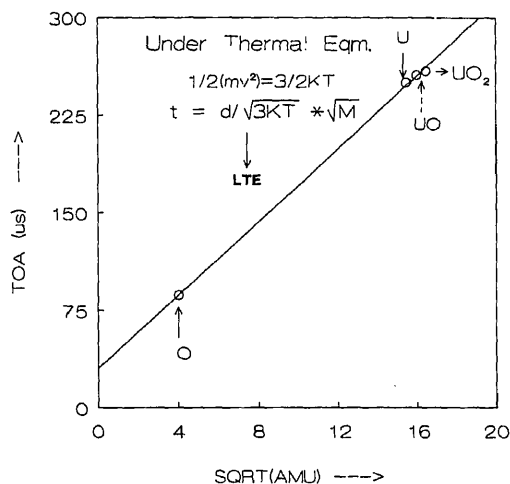


Figure 9. Dependence of TOA for O, U, UO, UO₂ vapour species as a function of their molecular weight (square root).

Once the existence of thermal equilibrium is established, then there should be an equilibrium surface temperature. The molecular composition in the expanded beam is the same as that of the composition at the surface. Hence, if the surface temperature is known, then the partial pressure of the vapour species can be determined by the relation,

$$p_i = KI_i T,$$

where p_i and I_i are the partial pressure and intensity of the species i , and K the calibration constant. Physical measurement of surface temperature for the interaction of laser pulses of nanosec duration is beyond the state of art. Hence indirect methods are employed, such as the comparison of TOA of the species of the system with that of a relatively well studied reference such as graphite (Hastie *et al* 1988b). For example, if t_c is the TOA of C₂(g) over the graphite (reference) sample having a surface temperature T_g and t_u is the TOA of UO₂(g) over the UO₂ sample with a surface temperature, T_u , then under identical experimental conditions,

$$T_u = T_g^* (t_u / \sqrt{M_u}) / (t_c / \sqrt{M_c}),$$

where M_u and M_c are the molecular weights of UO₂(g) and C₂(g) respectively. Such studies on the determination of temperature and pressure are in progress.

6. Other applications

Though the primary motivation for building an LIV-MS system in our laboratory was the experimental determination of the equation of state of reactor fuels, sufficient flexibility was built into the experimental assembly so that it can be used in a variety of applications. Some of these are indicated below.

The results reported are based on a quadrupole mass spectrometer. In addition to this a reflection type time-of-flight mass spectrometer (TOFMS) is under construction for incorporation into the system. TOFMS has several inherent advantages such as pulsed operation, the acquisition of the entire spectrum for every laser pulse, high resolution, large mass range and high transmission.

In a linear TOFMS (Wiley and McLaren 1955), the resolution is limited on account of the energy spread of the ion packet. In the reflection type TOFMS (RTOFMS), which was originally developed by Mamyrin *et al* (1973), the resolution was improved to several thousands. This is achieved by reflecting the ions back by means of an appropriate grid of electrodes. The ions with the same m/e ratio but larger in kinetic energy penetrate deeper into the reflecting field and take longer time to turn around than ions of lower energy. The electrostatic potentials are adjusted so that the fast ions lag behind the slow ions after reflection, but catch up with the slow ions at the point of detection after the second drift region. Thus by compensating for kinetic energy spread, bunching (narrowing down the spread in the arrival time), of ions of each mass-to-charge ratio is achieved at the detector. We have designed such a RTOFMS (see figure 10) and this will be put into use shortly. The incorporation of RTOFMS in the LIV-MS system significantly extends the range of application of this experimental facility. Some of these applications are indicated below.

6.1 Cluster studies

Clusters represent an intermediate state of matter between small molecules and the condensed phase. Research in the chemistry and physics of clusters is currently developing at a rapid pace. It was the introduction of laser vapourization technique for the production of supersonic metal cluster beams by Smalley and co-workers (Kroto *et al* 1985), that led to the discovery of fullerenes. There is a considerable interest in the scientific world in studying gas phase metal clusters in order to

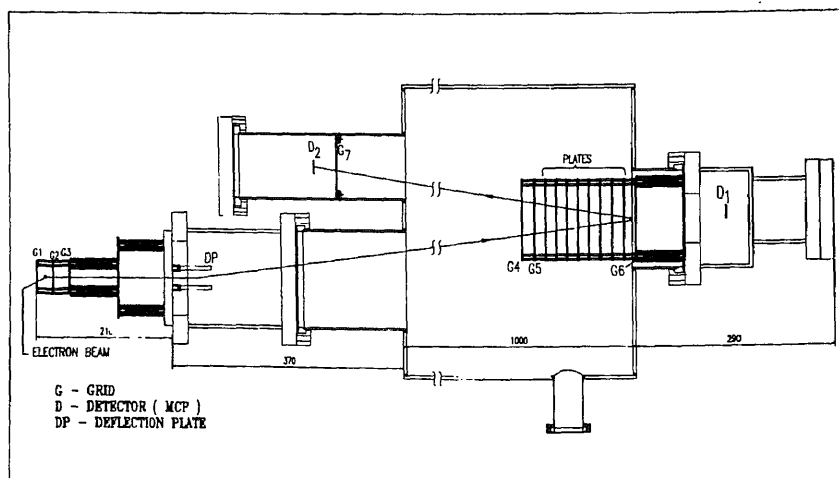


Figure 10. Schematic of reflection time-of-flight mass spectrometer (RTOFMS).

understand the nature of bonding, electronic structure and a host of other properties. In particular there is a strong interest in the variation of electronic structure, especially the band gap, from small clusters to the condensed phase.

One method of generating clusters of refractory materials is to vapourize the material by means of a pulsed laser and to sweep the resulting plume by means of an inert gas stream adiabatically expanding from high pressures through a molecular beam valve. Combined with a high resolution, high mass range mass spectrometer such a system can be used to study a wide range of clusters. The laser-TOFMS system is being used extensively in these type of studies. For example, when graphite was vapourized by a laser beam, the largest cluster size observed was C_9 (Hastie *et al* 1988b) (with C_3 being the major species). But, in the same vapourization experiment, when the plume was swept by a He gas jet, much larger clusters were observed, the most dominant of them being C_{60} and C_{70} (O'Brien *et al* 1988). Buckminsterfullerene or C_{60} , which has been the subject of extensive research, was identified to be orders of magnitude more abundant than all other clusters of atoms. Metal clusters show remarkable stability at magic numbers. Both metal and semiconductor clusters are under investigation with a view to understanding the transition from cluster to bulk behaviour like metallic or semiconductor properties. Our LIV-MS system is equipped with a pulsed molecular beam valve to enable us to take up cluster studies.

6.2 Surface analysis

The measurement of the local chemical composition at the surfaces and interfaces are currently being done using techniques such as Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS). The practical limitation of these techniques, namely, sensitivity (AES) and matrix effect (SIMS) are overcome, to a larger extent, by the recently reported surface analysis by laser ionization (SALI) technique (Welkie *et al* 1990). In SALI a monolayer of the sample surface is sputtered or desorbed by a probe beam (ions, electrons, laser) and a UV laser beam is directed through the plume of the sputtered neutrals, immediately above the sample surface, so as to obtain saturated ionization. Because ions are produced by a pulsed laser, subsequent mass analysis is done by TOFMS. Hence with minor modification in the experimental configuration, our system can be used for such chemical mapping studies.

6.3 Thin film coating

For the preparation of thin films of refractory material, laser induced evaporation and deposition is a relatively simple and clean method. This method has many practical advantages (Sankur and Hall 1985). Preliminary experiments have been done to prepare a good quality tin oxide film, which has wide applications as a semiconductor sensor for the detection of inflammable gases.

When highly selective and sensitive detection of ions is required under almost background-free condition, we can use resonance ionization mass spectrometry (RIMS) (Nogar *et al* 1985). This LIV-MS facility can also be used for the analysis of macro molecules such as proteins, peptides etc by using the matrix assisted laser desorption and ionization (MALDI) (Karas and Hillenkamp 1989) method.

7. Conclusions

Theoretical and experimental approaches to obtain the equation of state of refractory materials like reactor fuels at very high temperatures are discussed. Theoretical models have given results which can be used for making an estimate of the behaviour of reactor fuels under hypothetical core disruptive accidents. An experimental facility based on laser induced vapourization combined with mass spectrometry has been set up to generate the vapour pressures of these materials in the temperature range 2500–5000 K. Preliminary results are presented. Possible application of this facility in many other fields of research such as materials science and engineering are indicated.

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Studies on electrical conduction in $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$

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S V SURYANARAYANA

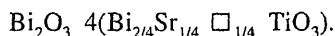
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Abstract. The ferroelectric $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$ has been synthesized and a study of the electrical (AC) conductivity was made on both poled and unpoled samples in the frequency range from 100 Hz to 1 MHz and from room temperature to 550°C. In the case of unpoled samples the activation energy was found to be 0.54 eV and subsequent to poling it was lowered to 0.39 eV indicating an increased conductivity after poling. Further the conductivity increased with increasing frequency and temperature. DC conductivity measurements were also carried out. Dielectric measurements indicate a peak in the dielectric constant at 530°C.

Keywords. Ferroelectrics; electrical conductivity; poling; dielectric constant.

1. Introduction

The materials with the generic formula $\text{Bi}_2\text{M}_{n-1}\text{R}_n\text{O}_{3n+3}$ (where $\text{M} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$ and Pb^{2+} and $\text{R} = \text{Ti}^{4+}, \text{Nb}^{5+}$ etc. ($n = 1, 2, 3, 4, 5$)) belong to a large family of layered structure compounds (Auruvillius 1949). With $n=4$ and M site being occupied by Bi_2^{3+} and Sr^{2+} and R with Ti^{4+} one can synthesize the compound $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$. The compound is tetragonal with slight orthorhombic distortion. Their a and b axes lie along $\langle 110 \rangle_c$ where the suffix denotes the cubic perovskite subcell so that $a \approx b \approx 2a_c \approx 0.54$ nm. The c axis is inherently long. These layered perovskite compounds are ferroelectric with high Curie temperatures (Subba Rao 1962). The ionic polarization makes an important contribution to the permanent dipole in the ferroelectric state. The structural consequence of this polarization is to distort the octahedral coordination, and thereby to lower the crystal symmetry. For the present system the molecular formula can also be written as (Chen Da Ren 1986),



The latter part has an ABO_3 type perovskite structure but the ions in the A position are different. The occupancy of A site is 2/4 Bi, 1/4 Sr and 1/4 $\square$ vacancy. The number of Bi^{3+} ions in the perovskite layer is twice as much as that of the Sr^{2+} ions. Chen Da Ren and Guo Yan Yi (1982) reported piezoelectric properties of a number of compounds by replacing the cations having similar structural configurations. According to them the Bi^{3+} ion has an important effect on the bond strength of $\text{Ti}^{4+} - \text{O}^{2-}$ (along a axis) in the compound $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$. The low crystal symmetry and high coercive fields observed in these compounds, result in the high stability of the piezoelectric properties for ceramic materials of $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$ either under high temperature or under one dimensional stress. Such compounds are important for many applications involving piezoelectric properties of ceramics. $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$ has been tested recently for SAW device applications (Takenaka *et al* 1983).

It has been found that these ceramics with Bi-layer structure, owing to their very high coercive fields and lower symmetry may have an essentially weak point in that a satisfactorily large remanent polarization cannot be obtained by poling. To solve this problem, different methods of preparation of the compounds have been suggested viz. hot forging, hot rolling, hot extrusion and superplastic deformation. These methods give ceramics with grain orientations and different densities (Takenaka *et al* 1975). The present workers have felt that different preparation methods give compounds with different electrical conductivities. According to Gurevich (1971) the difference in the numerical values of the Curie constant determined by different authors, for ferroelectrics is far beyond the experimental errors and is due to the different electrical conductivities of the crystals. The conductivity appreciably affects the domain structure and its motion. The preparation of single domain crystals is dependent upon the competition between the rate of growth of the ferroelectric phase and variation in the concentration of the free charge carriers. When the crystal shifts from para to the ferroelectric phase, it has been found that the electrical conductivity appreciably restricts the utilization of several properties of ferroelectrics. For example, polarized ferroelectric ceramics should have piezoelectric properties up to the Curie point, but experimentally, many of the piezoelectric transducers suffer from the degradation of piezoelectric properties at temperatures much below this temperature. Due to the very strong increase in the electrical conductivity with rise in temperature it is not possible to polarize the ferroelectric ceramics near the Curie point and at the same time utilize the potentialities of the ferroelectric ceramics (Gurevich 1971). Therefore the study of electrical conductivity becomes an important aspect. The present workers have undertaken the study of conductivity of $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$ prepared by the double sintering method. The technique selected is that of the study of impedance by an impedance analyzer to analyze the AC conductivity. The DC conductivity has also been studied. The capacitance measurements have been made to assess its dielectric anomaly. The results are presented here.

2. Experimental

2.1 Sample preparation

The polycrystalline samples of $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$ were prepared by the method of reactive sintering. The standard ceramic fabrication procedure has been followed for the preparation. The initial compounds SrCO_3 , Bi_2O_3 , TiO_2 (AR grade) were mixed in appropriate ratios as required by the balance equation for the synthesis of the desired compound. The mixture was thoroughly ground and the particle size of the initial materials ranged from 1–2 μm . The mixture was stacked in a crucible and sintered isothermally in air at 850°C for 2 h and then cooled. Pellets having a diameter of 1 cm and thickness of 1–2 mm, were made by applying a pressure of 8 MPa. The pellets were subjected to thermal heating at 400°C for 2 h to eliminate the binder (polyvinylalcohol) and finally sintered at 1200°C for densification. The pellets were cooled slowly from 1200°C–1000°C and then allowed to furnace cool. The entire sintering was done in a microprocessor-based furnace. The densified pellets were used for all measurements. The density of the pellets was found to be 89% of the X-ray density.

2.2 Characterization and measurements

The single phase formation was confirmed by XRD. The electrical measurements in the frequency 100 Hz–1 MHz were made using an HP4192 A impedance analyzer interfaced to a computer in the temperature range from room temperature to 550°C. The larger faces of the pellets were initially coated with silver paint and dried at 100°C.

The DC conductivity data was evaluated by measuring the resistance in the sample under a DC bias using the two-probe method at various temperatures on a Keithley 610C electrometer.

Electrical (AC) conductivity (using the admittance method) measurements were carried out on the silver coated pellets by placing them in between two stainless steel blocks which in turn were connected to the leads. The frequency range used was 100 Hz–1 MHz and the measurements were carried out in the temperature range from room temperature to 550°C.

3. Results and discussions

3.1 Electrical conductivity

The specific conductivity in air was deduced from the admittance values and the results are shown in figure 1. The pellet used was an unpoled sample. At the initial temperatures above room temperature the admittance decreases up to about 150°C while at temperatures above this value, the conductivity increases with the rise in temperature as well as with frequency. The $\log \sigma$ vs $10^3/T$ plots shown in figure 1 indicate the behaviour of the sample with the frequency of the AC signal and the temperature. The activation energy from this plot comes out to be 0.542 eV (at 500 kHz). The conductivity increases with frequency (figure 2) and this dependence can be expressed as (Yootarou *et al* 1973)

$$\sigma' = A \cdot \omega^n, \quad (1)$$

where A is a constant, ω the angular frequency and n a number (0.546 at 400°C). From the Arrhenius plots shown in figure 1 it is evident that in the low temperature region the conductivity variation at different frequencies is less dependent on temperature. The difference in frequency dependence of conductivity is more prominent at low temperatures. The activation energy as determined in the high temperature regions of the plots decreases with the increase in frequency.

The impedance data was also taken on the sample poled electrically. The electric poling was done placing the silver coated sample in an oil bath in between two electrodes to which an electric field of 10.6 kV/cm was applied. The sample was heated in the presence of an external field to 150°C and it was poled at this temperature in the presence of the field. The field was retained while cooling as well. The surface charges were removed by rubbing the sample with a shorted metal foil. The sample was then inserted in the sample holder and the impedance data collected. It was noticed that the poled samples showed higher conductivity values (figure 3) than the unpoled samples. The activation energy for a poled

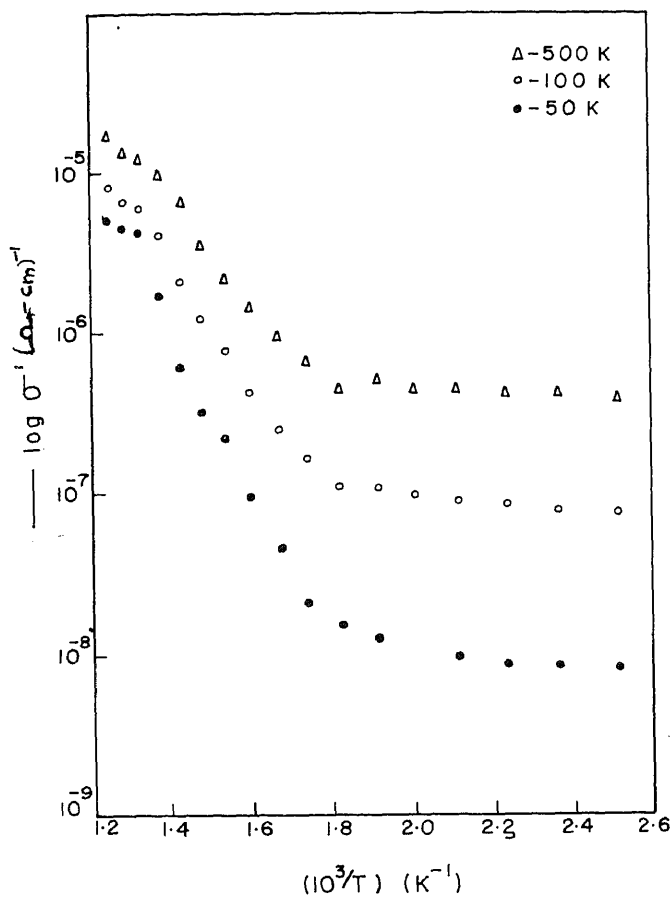


Figure 1. Variation of $\log \sigma'$ with $1/T$ for an unpoled sample.

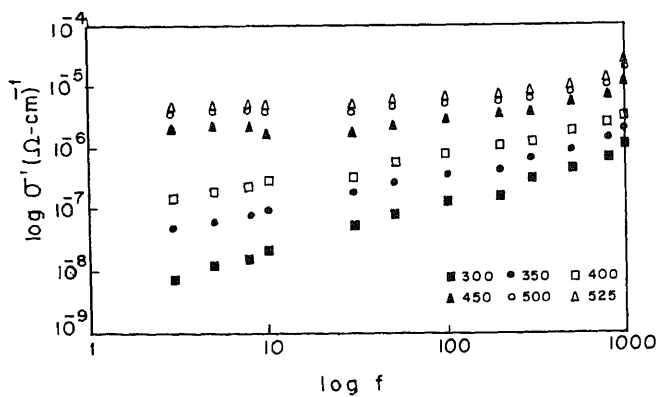
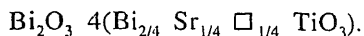


Figure 2. Variation of $\log \sigma'$ with frequency.

sample in the high temperature region (0.39 eV) comes out to be less than that in the unpoled sample (0.54 eV). Further the activation energy as determined from the Arrhenius plots (figure 4) for DC measurements has been found to be 1.52 eV which is more than that for AC conduction in the same temperature region. The DC conductivity increases monotonously with temperature. As mentioned earlier for $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$, the molecular formula can be written as



Therefore there is a vacancy in the A position, in the perovskite structure of ABO_3 type, which will also contribute towards conductivity. The values of activation energies also suggest this. In the poled sample we get a higher AC conductivity and as the temperature is increased, there will be a depletion of polarized charges, contributing to higher conductivity values. This is obvious from the experiment which shows that above the transition temperature, the value of σ reaches the same values as those of the unpoled samples. The sample cannot be poled at higher

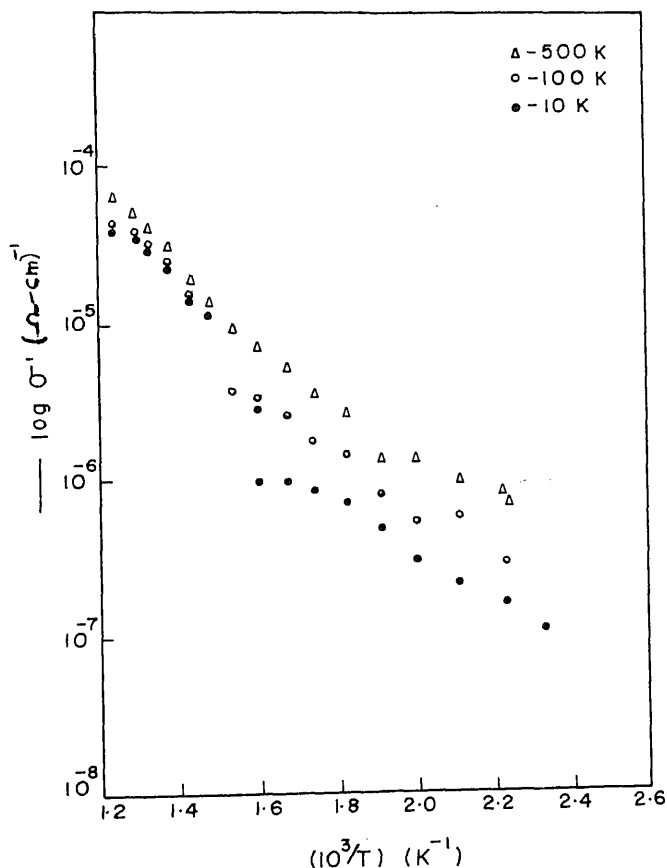


Figure 3. Variation of $\log \sigma'$ with $1/T$ for a poled sample.

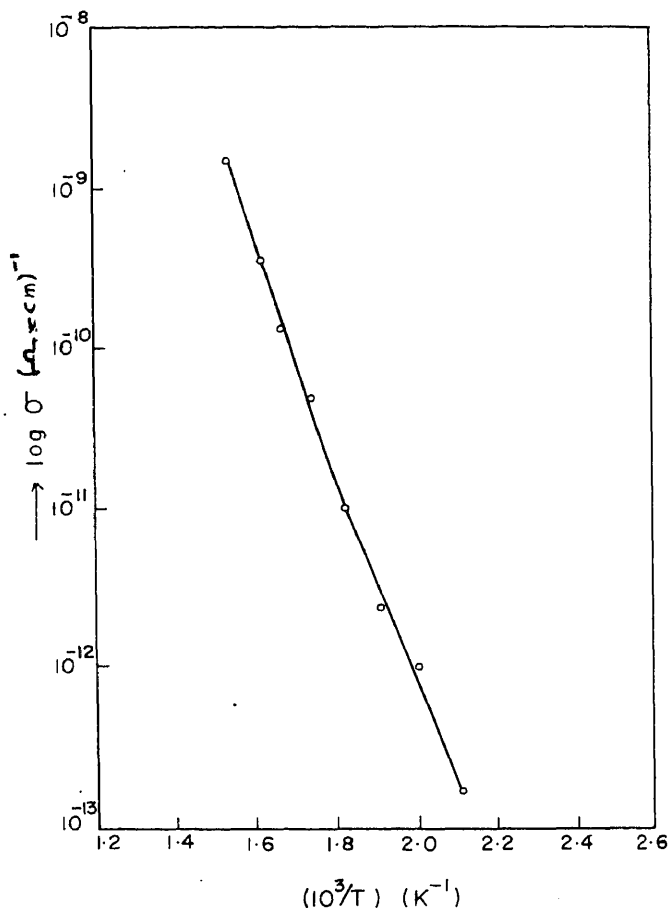


Figure 4. Variation of $\log \sigma_{dc}$ with $1/T$.

temperatures on account of its high conductivity at those temperatures. Further the poling process in turn depends upon the density of the sample prepared.

3.2 Dielectric measurements

The capacitance measurements were made on electrically poled samples with an impedance analyzer at different frequencies and in the temperature range from room temperature to 600°C. Figure 5 represents the observed variation of dielectric constant with temperature as a function of frequency. It was found that at low frequencies the dielectric constant increased with temperature even beyond the T_c . This may be due to the fact that at lower frequencies the contribution of electrical conduction of the sample is more, leading to the masking of the dielectric peak at the transition temperature but at higher frequencies, apart from the dispersion a peak is observed at around 530°C. The values of permittivity are fitted into the Curie-Weiss law

$$\varepsilon = C/(T-T_c),$$

where ε is the dielectric constant, C the Curie constant and T_c the transition temperature. T_c has been found to be 528°C and the Curie constant comes out to be $0.37 \times 10^4 (^\circ\text{C})$. Figure 6 depicts the variation of $\tan \delta$ as a function of both temperature and frequency. The value of $\tan \delta$ increases appreciably before T_c . It decreases with increasing frequency at higher temperatures and the peak in $\tan \delta$ becomes broader. The peak indicates the ferroelectric relaxation.

4. Conclusions

The results of investigations on sintered pellets indicate that the poled and unpoled samples behave differently *vis-a-vis* their conductivities. It was found that the unpoled samples exhibit lower conductivity values under both AC and DC conditions,

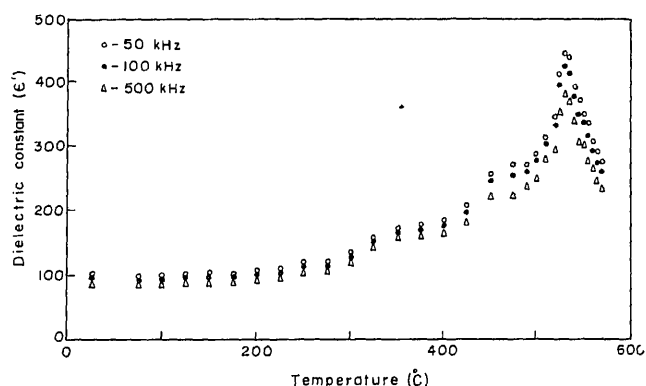


Figure 5. Variation of dielectric constant with temperature at different frequencies.

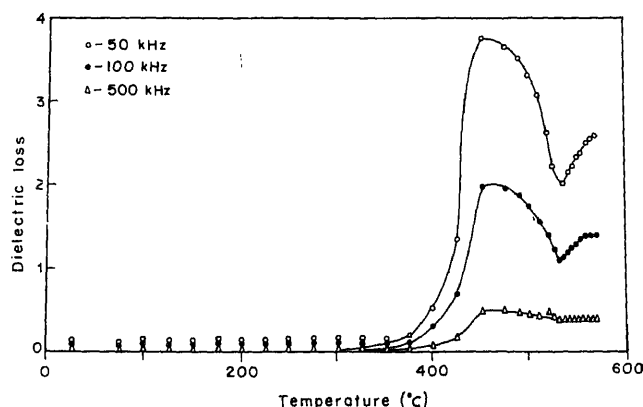


Figure 6. Variation of dielectric loss with temperature.

as compared to their poled counterparts. The converse was found to be true in the case of their activation energies. In so far as the dielectric transition is concerned, a peak was observed at 530°C which is well in agreement with the reported values. This piezoelectric ceramic is therefore suitable for use as a transducer material even at high temperatures on account of the fact that it has a high Curie temperature, low dielectric constant and a fairly stable behaviour at high temperatures.

Acknowledgements

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Photoelectrochemical studies on the mixed oxides, $A_6Nb_8Ti_2O_{30}$ ($A = Ba, Sr$)

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Abstract. The photoelectrochemical behaviour of oxide bronzes of the type $A_6Nb_8Ti_2O_{30}$ ($A = Ba, Sr$) has been studied. They show good photoactivity with photopotentials of the order of 700-800 mV. The flat band potential has been estimated to be -0.9 V vs SCE. The band gap estimated from the spectral response is 3.1 eV.

Keywords. Photoelectrochemical cells; titanates; niobates; oxide bronzes.

1. Introduction

Of the various oxides that have been studied as semiconductor photoelectrodes for the photoassisted electrolysis (PAE) of water, the mixed oxide titanates and niobates have proved to be excellent candidates (Wrighton *et al* 1976; Kung *et al* 1977; Hormadaly *et al* 1980; Subba Rao *et al* 1984; Matsumoto *et al* 1986; Paranthaman *et al* 1986). The main features of all titanates and niobates are the large negative flat band potential and their remarkable stability in strong acidic/alkaline solutions. The large negative flat band potentials (V_{fb}) result from the low electronegativity of Ti and Nb (1.5 for Ti and 1.6 for Nb, according to Pauling's scale). Because of the large V_{fb} , electrolysis of water is possible with a little applied bias. It has been demonstrated that with n -SrTiO₃ (Wrighton *et al* 1976) and n -Zn₂TiO₄ (Matsumoto *et al* 1986), it is possible to electrolyse water without any applied bias. The stability of these oxides in aqueous solutions is due to the fact that the photoanodic decomposition potentials of these oxides are more positive compared to $E(O_2/H_2O)$, especially at higher pH values. In most of these oxides, electronic conductivity can be induced easily (and hence the material can be made n -type) either by H₂ reduction or by suitable substitution (e.g. La substitution in SrTiO₃). The n -type conductivity arises from the Ti³⁺ $3d^1(t_{2g})$ or Nb⁴⁺ $4d^1(t_{2g})$ electronic levels which act as shallow donor centres. The only disadvantage of these oxides is their large and indirect band gap (usually > 3 eV). Because of the large band gap, these materials can absorb only the UV light, which constitutes only 3% of the solar spectrum. The indirect nature of the fundamental absorption leads to low absorption coefficient. Attempts to induce absorption in the visible region by substitution at Ti site with Cr, Ni etc were only partially successful. However, these ions lead to localized sub band gap levels, which act as recombination centres and thus give lower quantum efficiencies of light conversion.

Studies on various titanates and niobates have shown that the photoactivity of these compounds can be uniquely attributed to the presence of TiO₆ and NbO₆ octahedra. Since the photoelectrochemical (PEC) properties are influenced mainly by the band gap and the flat band potential and since these parameters depend on

the structure, search for new mixed oxide titanates and niobates with various structures is essential. Toward this end, we have chosen a series of oxide bronzes and have carried out PEC studies on them. Our earlier studies (Ramakrishnan *et al* 1993) on the hexagonal oxide bronzes, $\text{Ba}_3\text{Nb}_4\text{Ti}_4\text{O}_{21}$ have shown that they could be potential candidates for use as semiconducting electrodes in PEC cells. Presently we report our studies on the oxide bronzes of the type, $\text{A}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ ($\text{A} = \text{Sr}, \text{Ba}$). These compounds crystallize with a tetragonal bronze structure with space group $P4bm$. The lattice constants of these compounds are $a \sim 12.5 \text{ \AA}$ and $c \sim 4 \text{ \AA}$. Single crystal structural analysis on $\text{Ba}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ was reported by Stephenson (1965). The lattice is constructed of MO_6 octahedra joined by corners, every oxygen atom thus being common to two M atoms. The TiO_6 and NbO_6 octahedra are statistically distributed. The dielectric properties have been extensively studied in the literature (Jamieson *et al* 1969; Itoh *et al* 1970; Ikeda *et al* 1971; Itoh and Iwasaki 1973; Varaprasad 1985; Neurgaonkar *et al* 1988, 1990; Choudhary *et al* 1993). The compounds are reported to be ferroelectric with $T_c = 518 \text{ K}$ for $\text{Ba}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ and 403 K for $\text{Sr}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$. However the PEC behaviour of these compounds has not been explored. In the present study, we have carried out PEC studies on these phases, since these phases contain photoactive $\text{NbO}_6/\text{TiO}_6$ octahedra. Present results show that the photoelectrochemical behaviour of these compounds is comparable to that of the well known SrTiO_3 and TiO_2 .

2. Experimental

Polycrystalline $\text{A}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ ($\text{A} = \text{Sr}, \text{Ba}$) were synthesized from high purity BaCO_3 , SrCO_3 , TiO_2 (all of Cerac, UK) and Nb_2O_5 (99.9%) (SMP, Hyderabad). Stoichiometric

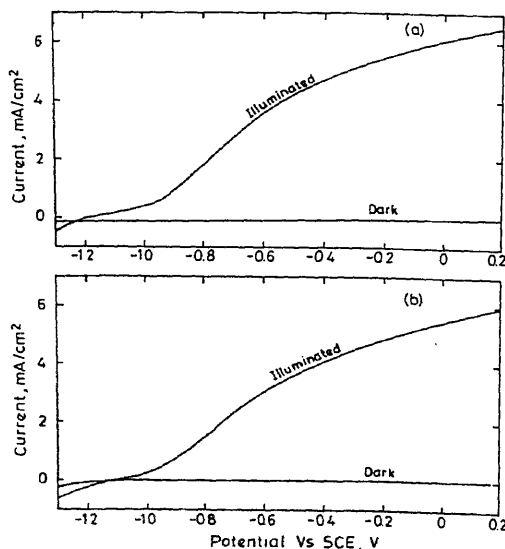


Figure 1. Potentiostatic current-voltage curves of the cell, (a) $n\text{-Ba}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}/1 \text{ M NaOH/Pt}$ and (b) $n\text{-Sr}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}/1 \text{ M NaOH/Pt}$ (1000 W Xe lamp; full intensity $> 1.5 \text{ W/cm}^2$).

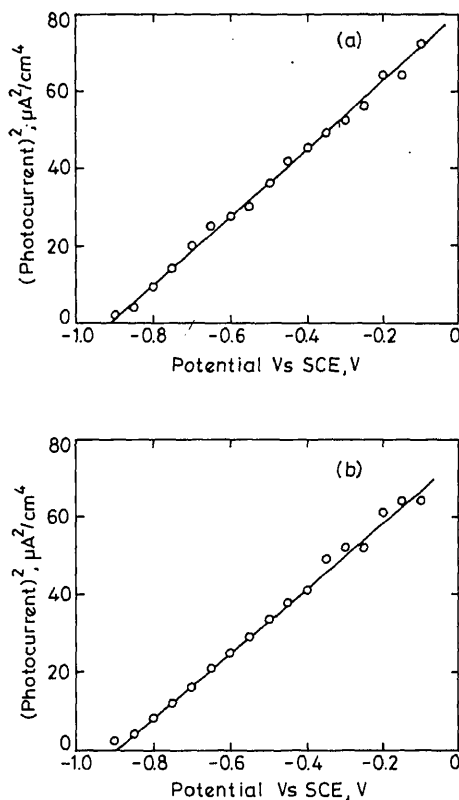


Figure 2. Flat band potential, V_{fb} , determination from I_{photo}^2 vs V plot for (a) $\text{Ba}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ and (b) $\text{Sr}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$. Data taken at 370 nm using monochromator. The data points are LSQ fitted to extrapolate to V_{fb} .

amounts of the oxides/carbonates were thoroughly mixed in an agate mortar and heated in air at 1473 K for 72 h with two intermittent grindings. The reacted powders were pressed into pellets (8 mm dia, 1–2 mm thick; WC lined SS die; hydraulic press: 3 tonnes) and sintered at 1473 K for 24 h and at 1623 K for 6 h. Phase formation was checked by using a computerized powder X-ray diffraction (XRD) unit (Rich Seifert, Germany; XRD 3000P, 35 kV; 30 mA; $\text{CuK}\alpha$ radiation). The compounds were reduced in H_2 atmosphere or by Ti gettering to induce electronic conductivity. PEC studies were carried out in aq. 1 M NaOH electrolyte. The preparation of the electrodes and electrolyte and the details of PEC experimental set-up are as described elsewhere (Ramakrishnan *et al* 1993). The working electrode (semiconductor electrode) was etched with 5% aqueous HF solution for 1–2 min before measurements.

3. Results and discussion

All compounds were single phasic in nature. The XRD patterns could be indexed

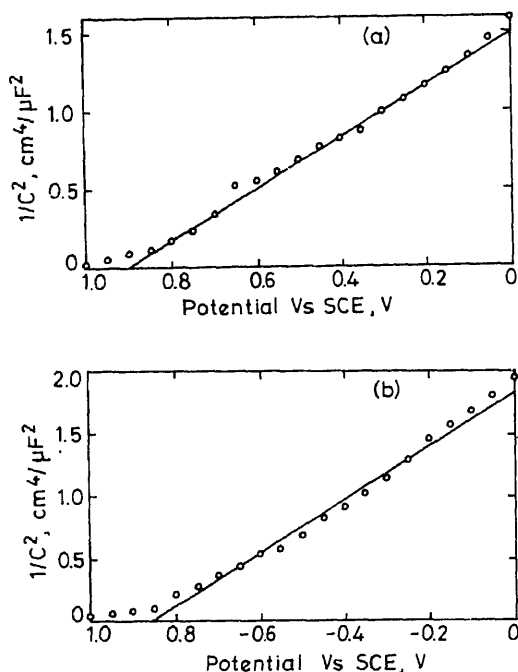


Figure 3. Mott-Schottky plots for (a) $\text{Ba}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ and (b) $\text{Sr}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ in 1 M NaOH solution.

LSQ fit of the high angle lines viz. $a = 12.353 \text{ \AA}$, $c = 3.99 \text{ \AA}$ for $\text{Ba}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ and $a = 12.447 \text{ \AA}$, $c = 3.86 \text{ \AA}$ for $\text{Sr}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$, agree well with those reported in the literature. Phases were stable upon reduction as confirmed by X-ray diffraction. The as-sintered pellets were white in colour and upon reduction they turned black indicating the creation of $\text{Ti}^{3+} 3d^1(t_{2g})$ and/or $\text{Nb}^{4+} 4d^1(t_{2g})$ levels. The room temperature resistivities of the reduced pellets were $\sim 10^2 \text{ ohm cm}$, while the unreduced pellets were insulators having resistivities $> 10^7 \text{ ohm cm}$.

Photopotentials were observed immediately upon irradiation of the electrode/electrolyte interface with negligible dark potentials. The shift in the potential upon irradiation was towards the negative direction indicating the n -type nature of the electrode. A maximum V_{oc} of the order of 700–800 mV was observed. Photocurrent (i_{photo}) stability plot at a potential of +0.2 V vs SCE shows i_{photo} of the order of 6 nA/cm^2 . Sharp rise and cut off in V_{oc} as well as i_{photo} before and after irradiation and the stability during illumination indicates good quality of the electrode and the absence of recombination centres in the space charge region.

The I - V characteristics for $\text{A}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ ($\text{A} = \text{Sr}, \text{Ba}$)/1 M NaOH/Pt, are shown in figure 1. The plots show negligible anodic dark current indicating the rectifying nature of the semiconductor-electrolyte interface. The photocurrent almost saturates above a potential of 0 V vs SCE, indicating fairly good absorption of light by the phases. The onset of the photocurrent was observed in the potential range -1.2 to -1.1 V vs SCE.

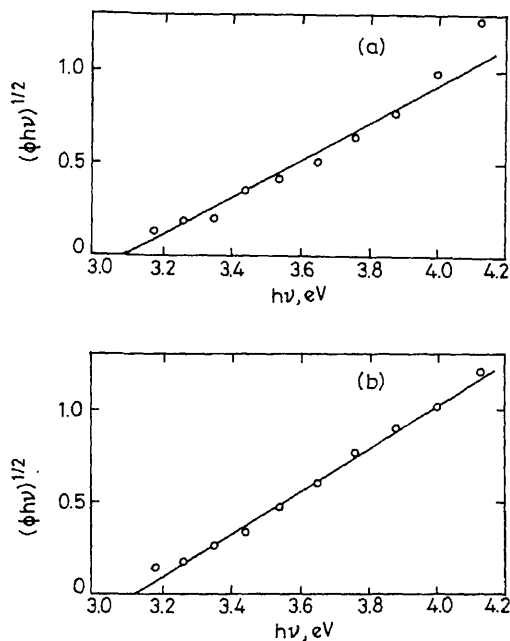


Figure 4. Determination of indirect band gap of (a) $\text{Ba}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ and (b) $\text{Sr}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ from the plot of $(\Phi h\nu)^{1/2}$ vs $h\nu$.

The flat band potentials were determined from the I - V characteristics using monochromatic radiation (350 nm) using the relation,

$$I_{\text{photo}}^2 \propto (V - V_{\text{fb}}). \quad (1)$$

Figures 2a and b show the I_{photo}^2 vs V (vs SCE) plot for $\text{A}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ ($\text{A} = \text{Ba}$ and Sr respectively). The linear plot obtained by the LSQ fit of the data points extrapolate to an identical V_{fb} of -0.9 V vs SCE for both the compounds. The flat band potentials were also estimated from the Mott-Schottky plots using the Mott-Schottky equation, viz.

$$1/C^2 = (2/\epsilon\epsilon_0 qN_D) [(V - V_{\text{fb}}) - (kT/q)], \quad (2)$$

where, k is the Boltzmann constant and T the absolute temperature. Hence, $1/C^2$ is directly proportional to the applied potential at a given temperature and the extrapolation of the linear plot of $1/C^2$ vs V gives the flat band potential. The values of the flat band potential obtained from Mott-Schottky plot are -0.9 V vs SCE for $\text{Ba}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ and -0.855 V vs SCE for $\text{Sr}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ (figure 3). This slight shift towards positive value for the Sr analogue is not observed in the values obtained from I^2 vs V (vs SCE) plot which gave identical value of -0.9 V vs SCE. These values of flat band potentials are more positive than that of SrTiO_3 (-1.3 V vs SCE) and TiO_2 (-1.0 V vs SCE).

Photocurrents were measured as a function of wavelength at an applied bias of +0.2 V vs SCE, using Jobin-Yvon monochromator. The measured I_{photo} values were normalized to the input light flux as measured by a thermopile and the quantum efficiency (Φ) values were calculated. Quantum efficiencies of about 50% were observed for lower wavelengths which are comparable to that observed for SrTiO_3 and the quantum efficiency decreased to low values at wavelengths > 380 nm. According to Gartner's model, the quantum efficiency, Φ , is related to the energy of photons ($h\nu$) by the equation

$$(\Phi h\nu) \propto (h\nu - E_g)^{n/2}, \quad (3)$$

where $n=1$ for direct band gap and $n=4$ for indirect band gap. Thus, the band gap and its nature can be found by extrapolation of the linear portions of $(\Phi h\nu)^{2/n}$ vs $h\nu$. Indirect band gap (E_g) values of 3.10 and 3.12 eV were estimated from $(\Phi h\nu)^{1/2}$ vs $h\nu$ plot for the Ba- and Sr-analogues respectively (figure 4). The observation of near identical band gap for both the compounds is due to the fact that the bottom of the conduction band is constituted of Ti/Nb orbitals and the A-ion has negligible influence in spite of the structural similarity. However, the ferroelectric Curie temperature (T_C) values differ indicating the covalency effects of the A-O bond w.r.t. Ti-O and Nb-O bonds. Sr-O bond is more covalent making Ti-O/Nb-O bonds more ionic in $\text{Sr}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ and thereby reduced T_C .

4. Summary

The oxides $\text{A}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ ($\text{A} = \text{Sr}, \text{Ba}$) have been studied for the first time as photoanodes. They show good photoactivity and stability in strong alkaline solution. They have a fairly large negative flat band potential of -0.9 V vs SCE and hence it is possible to electrolyse water with a little applied bias. They have a wide band gap of 3.1 eV. However, the structure provides ample scope for manipulation of band gap by chemical substitutions and these studies are underway.

Acknowledgement

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A new chemical route for the preparation of fine ferrite powders

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Abstract. Precursors to MFe_2O_4 [spinels ferrites; where $M = Ni(II), Co(II)$ and $Zn(II)$] have been prepared by the evaporation of polyvinyl alcohol added mixed metal nitrate solution, in presence and absence of urea. The precursor materials have low ignition temperature and are spontaneously combustible at low temperatures ($250^\circ C$ to $400^\circ C$). The heat liberated through the process is sufficient for the crystallization of the desired ferrite phase. The urea added process resulted in finer, superparamagnetic particles (12–17 nm) compared to the process without urea (particle size 25–30 nm). The ultrafine ferrite powders obtained have been characterized by X-ray powder diffraction (XRD), thermal gravimetry (TG), differential scanning calorimetry (DSC), infrared spectroscopy (IR), transmission electron microscopy (TEM) and room temperature magnetic measurement studies.

Keywords. Ferrites; chemical synthesis route; polyvinyl alcohol; urea; evaporation; fine particle; Powders.

1. Introduction

Technologically, fine-particle ferrites have been of interest due to their application in the preparation of high density ferrites at low temperatures, pigments and as catalysts (Leech and Campbell 1975). The surface properties and the microstructures of such powders, which control most parameters required for any particular application, often depend on the method of their preparation (Das 1981).

The conventional ceramic method for the preparation of ferrites, though successful for large scale production of bulk powders because of its low cost and easy adaptability, have several limitations (Johnson and Ghate 1985) in the production of fine powders. Long heating schedules and high temperatures, the requisites for the ceramic route, sinter the final product and result in the loss of the fine particle nature of the powders. The method is thus affected by a poor control of particle size, morphology and microscopic homogeneity.

The chemical synthesis routes for the production of fine ferrite powders have overcome many of the limitations of the ceramic method. The important chemical synthesis routes, which have gained substantial popularity over the years, include the precursor compound method (Patron *et al* 1987), the coprecipitation method (Schuele 1959; Pathak and Pramanik 1993), the sol-gel method (Marcilly *et al* 1970; Dishlich 1971), the solvent evaporation method (De Lau 1970; Anderton and Sale 1979), the hydrothermal method (Pannaparayil and Komarneni 1989) and the combustion method (Ravindranathan and Patil 1987). These methods are reported (Das 1983) to result in ferrite particles ranging from 10 to 100 nm.

Although several chemical routes exist for the preparation of fine ferrite powders, the considerations of affordability and versatility of a route still remain as a major challenge for the material scientists involved in the development of new synthetic routes.

In the present investigation, an attempt has been made to establish a new chemical route, which is both affordable and versatile, for the synthesis of fine mixed-oxide powders. In this paper, we report the preparation and characterization of only a class of the mixed-oxide powders, viz. the ferrites. The route involves rapid evaporation or spray drying of a polyvinyl alcohol (PVA) added mixed metal nitrate solution in the presence and absence of urea, followed by the pyrolysis of the evaporated or dried mass. The pyrolysis results in X-ray amorphous or, crystalline ferrite powders.

2. Experimental

2.1 Preparation of the precursor materials

To prepare the mentioned oxide systems appropriate amounts of the desired metal nitrates are taken into aqueous solution. 10% (w/v) aqueous solution of PVA (mol. wt. = 1,25,000) is then added to each of the mixed metal nitrate solutions so as to maintain a metal ion : vinyl alcohol monomer unit mole ratio of 1 : 2.5. In case of the urea added process, the urea (by weight) is introduced into the system, with thorough stirring, maintaining the urea to cation mole ratio at unity. The PVA helps the homogeneous distribution of the metal ions in its polymeric network structure and inhibits their segregation/precipitation from the solution. The resulting viscous liquid mixture of PVA metal nitrates is evaporated to dryness or spray dried between 130°C and 150°C to obtain a voluminous organic based fluffy precursor powder.

2.2 Formation of ultrafine ferrite powders

Ultrafine ferrite powders are obtained from the thermal decomposition of the carbonaceous precursor material. The heat liberated during the exothermic decomposition of the precursor powder facilitates the solid phase reaction between the constituent metal ions and results in the ferrite phase formation. The exothermic decomposition of the precursor material is accompanied by the evolution of various gases (CO, CO₂, H₂O). The evolution of gases not only helps the products to disintegrate but also helps to dissipate the heat of combustion, thus inhibiting sintering of the fine particles.

To study the influence of calcination temperature and time on the particle size, the precursor powders are calcined at varying heat treatment temperatures (between 400°C to 900°C) for varying periods of time (2 h to 24 h).

2.3 Physical measurements

Thermal gravimetric and differential calorimetric (TG/DSC) studies of the precursor material, produced by the PVA evaporation route in the presence and absence of urea, are done on the STA-625 thermal DSC. All experiments are performed in air atmosphere with a heating rate of 10°C/min. The infrared (IR) spectra for the precursor and the heat treated powders are recorded on the Perkin Elmer 883

infrared spectrophotometer from 400 to 4000 cm^{-1} by the KBr pellet method. The X-ray powder diffraction (XRD) patterns for the precursor and the heat treated powders are recorded using Phillips P.W. 1710 X-ray diffractometer with $\text{CuK}\alpha$ radiation and Nickel filter. Transmission electron microscopy (TEM) studies of the prepared powders are done on CM-12 Phillips electron microscope. A vibrating sample magnetometer is used for the room temperature magnetic studies of the prepared powders.

3. Results and discussion

The simultaneously recorded TG and DSC data for the NiFe_2O_4 , CoFe_2O_4 and ZnFe_2O_4 precursor powders produced by PVA added mixed metal nitrate solution evaporation method, in the presence and absence of urea, follow a similar trend. The thermograms reveal that the precursor powders, produced in the presence and absence of urea, both involve a single step decomposition between 200°C to 400°C . The precursor powders, in the absence of urea, are found to decompose between 210°C to 360°C with an exothermic peak at 302°C . The process involves an exothermic heat liberation of $280\text{--}24\text{ mcal/mg}$ with $16\text{--}64\%$ weight loss. The exothermic heat liberation is due to the combustion of the carbonaceous remains of PVA and the decarboxylation of the precursor material, which is accompanied by the evolution of gases such as CO , CO_2 and H_2O (water vapour). The thermal effects are thus accompanied by weight loss in TG curve. While the precursors, in the presence of urea, are found to decompose over a wider temperature region (between 190°C and 410°C) with an exothermic peak at 341.5°C . The heat liberated in the process is also higher (398.5 mcal/mg) and so is the weight loss ($18\text{--}64\%$). This is because, here the combustion of the carbonaceous remains of PVA is additionally accompanied by the decomposition of the organic residue from urea, which begins to decompose around 200°C . Hence, the exothermic heat generated is more, which is accompanied by larger amounts of gas evolution. This is manifested by higher weight loss in the TG curve.

IR spectra for all the precursor powders, prepared in the presence or absence of urea, are similar. The IR band at 3387 cm^{-1} and bending mode at 1619 cm^{-1} in the precursor material, could be due to the presence of moisture in the precursor material. The intensity of these bands diminishes and vanishes with the increase in heat treatment temperature. The absorption bands at 1394 cm^{-1} (strong), 1087 cm^{-1} (strong), and at 822 cm^{-1} (weak) in the precursor material, can be assigned to the various vibrational modes of the carboxylate ions. Since, during the complete evaporation process of the starting solution, the metal nitrates get decomposed in presence of the carbonaceous remains of the PVA and correspondingly carboxylate salts and oxides are expected to form. This absorption band disappears after heat treatment at 450°C . The absorption at 578 cm^{-1} and 420 cm^{-1} are due to the lattice absorption of NiFe_2O_4 (Grimes and Collect 1971). These bands increase in intensity with high heat treatment temperatures of the precursor powder.

The XRD of the powders, produced from the PVA evaporation route in presence of urea (figure 1), reveals that the precursor powders are X-ray amorphous. It also shows broad peaks of the corresponding ferrite phase for the precursor powders calcined at 450°C for the varying periods of time. This indicates the growth of

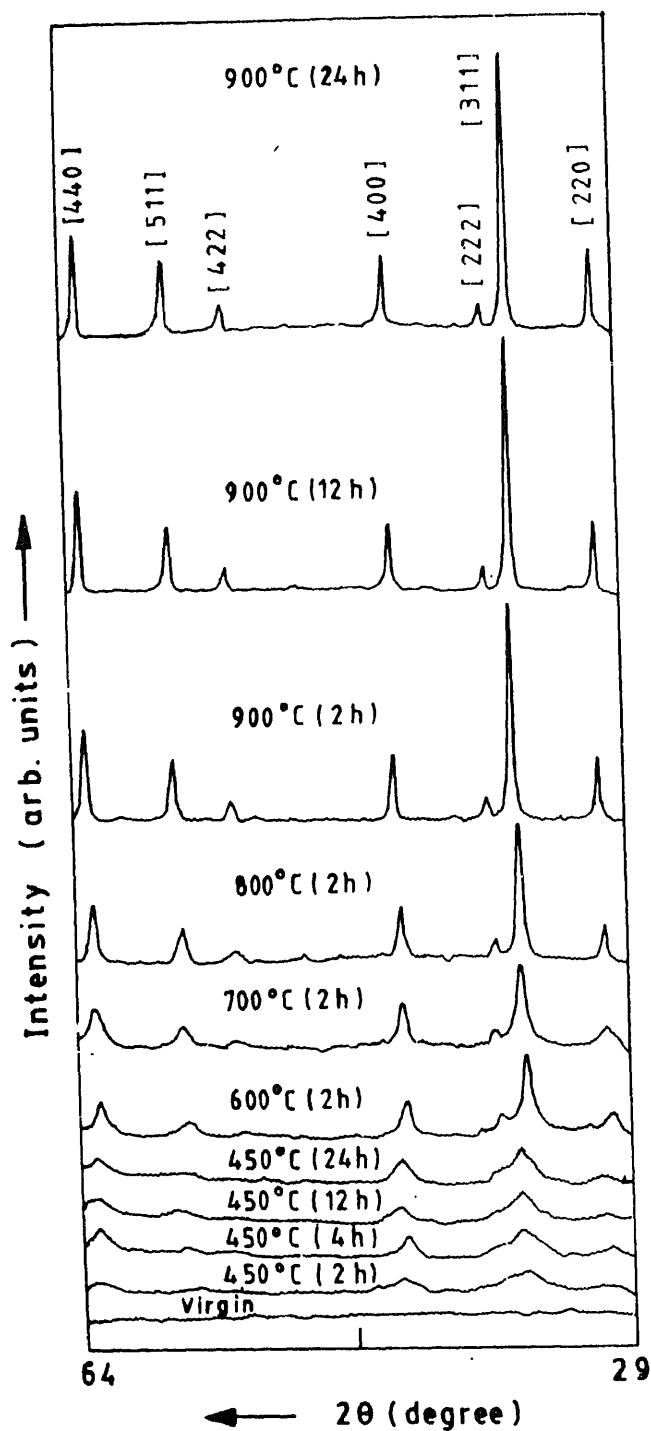


Figure 1. X-ray diffractograms of NiFe_2O_4 precursor powders, prepared in the presence of

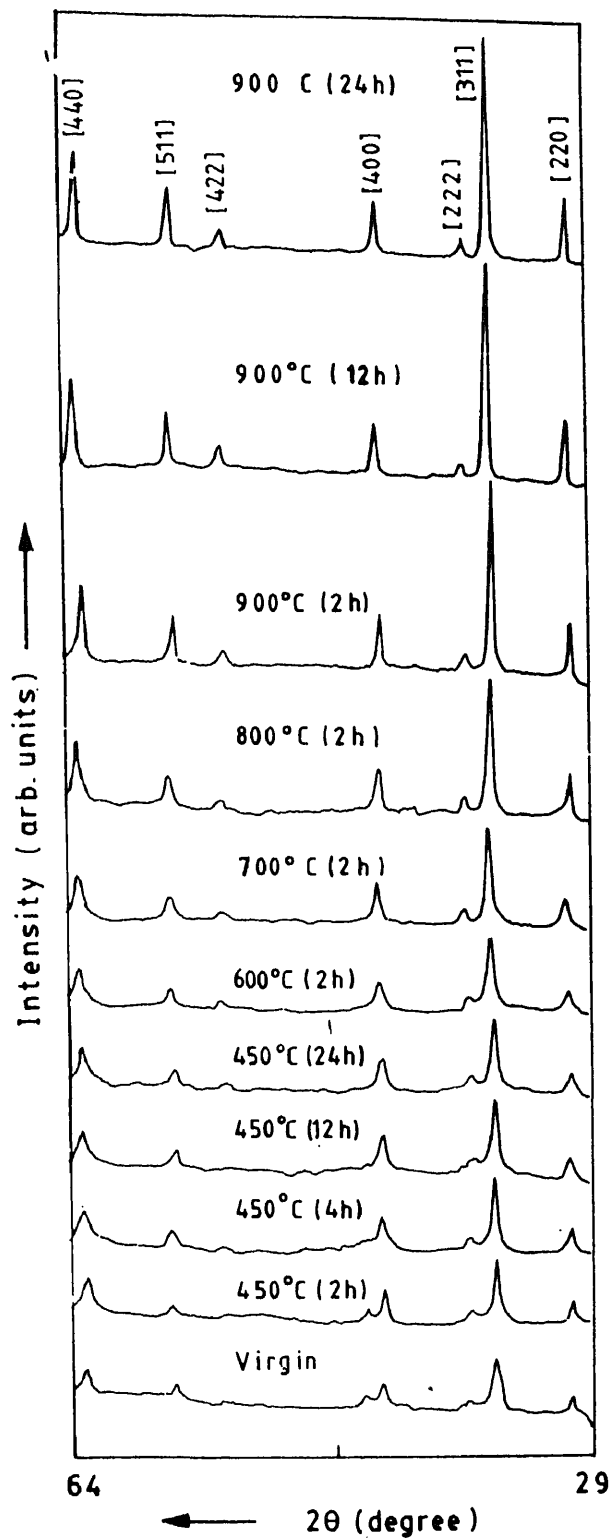


Figure 2. X-ray diffractograms of NiFe_2O_4 precursor powders, prepared in the absence of urea, with varying calcination temperatures and time.

crystallinity in the precursor powders after thermal decomposition at 450°C and with subsequent heat treatments. While XRD of the precursor powders, prepared in the absence of urea in the PVA evaporation route (figure 2), shows the formation of the corresponding ferrite phase before calcination. The XRD peaks, corresponding to the ferrite phase, increase in intensity with subsequent heat treatments. This indicates the growth of crystallinity in the powders with increase in heat treatment temperature and time.

The crystallite size of the prepared powders are determined from XRD line broadening using the Scherrers' equation (Klung and Alexander 1974). These studies reveal that with the increase in the calcination temperature the crystallite size gradually increases for all the powders. The crystallite size variation with calcination period, though has a linear increasing trend, is not very pronounced. It also shows that at low heat treatment temperatures (< 700°C), the powders prepared by PVA evaporation route in presence of urea, yield finer crystallites (~ 170 Å) compared to the crystallites (~ 245 Å) of the powder prepared in absence of urea. In addition, it is also found that on high temperature heat treatment, the powders prepared in both the presence and absence of urea, attain similar values of crystallite size (~ 350 Å). TEM studies support XRD line broadening results. TEM micrographs show that the low temperature (< 700°C) heat treated powders, prepared in presence of urea, result in finer particles compared to the powders prepared in the absence of urea. The average particle size (as observed from TEM) of powders, prepared in the presence of urea, after heat treatment at 400°C, is found to be between 12–17 nm (figure 3a). These powders show polycrystalline ring diffraction pattern in TEM (figure 3b), corresponding to the spinel structure indicating the fine particle nature of the powder. While, the average particle size of the powders, prepared in absence of urea and heat treated at 450°C, is found to lie between 25 to 30 nm (figure 4). These powders show single crystal diffraction pattern in TEM, corresponding to the respective spinel structure. High temperature (> 800°C) heat treatment of the same powders, prepared either in the presence or in the absence of urea, results in similar values of particle size (100 nm to 120 nm), as depicted in the TEM micrographs.

The room temperature magnetic studies reveal that the NiFe_2O_4 and CoFe_2O_4 powders, prepared in the presence of urea and heat treated at 450°C for 4 h, show superparamagnetic behaviour. While the powders prepared in the absence of urea are not superparamagnetic. Superparamagnetism is inferred by zero hysteresis in the B-H curve. The superparamagnetism observed in the powders vanishes when the same is heat treated beyond 500°C.

3.1 *The role of polyvinyl alcohol*

In the PVA added metal nitrate solution evaporation, the PVA plays a dual role.

(i) When the optimum amount of PVA is added to the mixed metal nitrate solution, the polar groups of the long chain of the polymer play a wrapping and covering role for the cations in the solution. As a result their mutual contact is avoided and so the cations do not grow in size. Thus the metal ions remain uniformly distributed in the viscous liquid during evaporation and their segregation and precipitation from the solution are avoided.

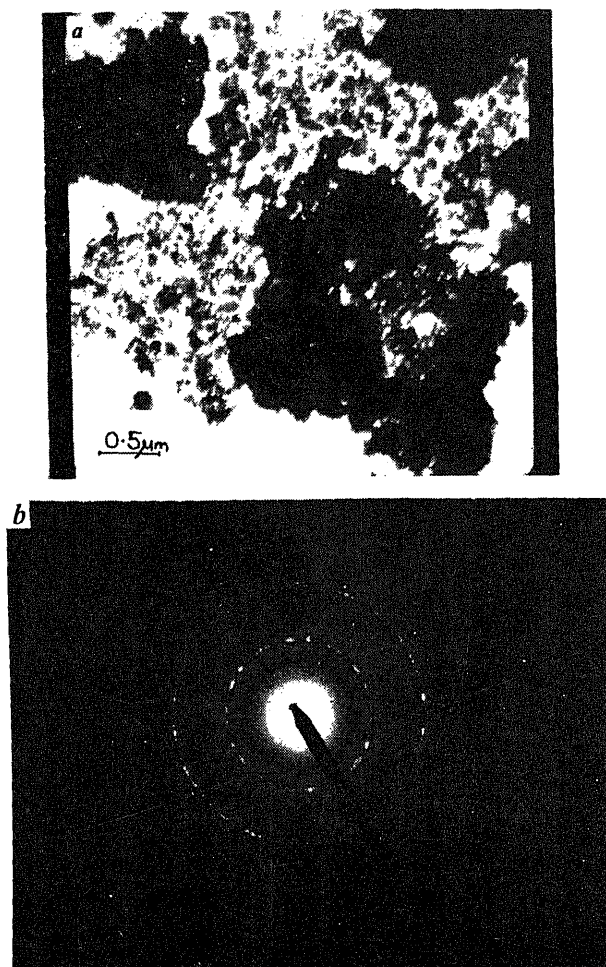


Figure 3. a. TEM micrographs of NiFe_2O_4 precursor powders, prepared in the presence of urea, after calcination at 450°C for 4 h and b. TEM diffraction of NiFe_2O_4 precursor powders, prepared in the presence of urea, after calcination at 450°C for 4 h.

(ii) The carbonaceous material, obtained from the complete evaporation of PVA, provide heat through combustion for the formation of fine single phase ferrite powders at a relatively low external temperature.

3.2 Role of urea

The addition of urea to PVA added metal nitrate solution, when evaporated to a pasty mass, acts as a retardant. It stops the crystallization of the precursor powder during complete evaporation of the PVA added solution. Moreover, the DSC studies reveal that the precursor powders, prepared in presence of urea, decompose over a wider temperature range compared to the precursor powders prepared in absence

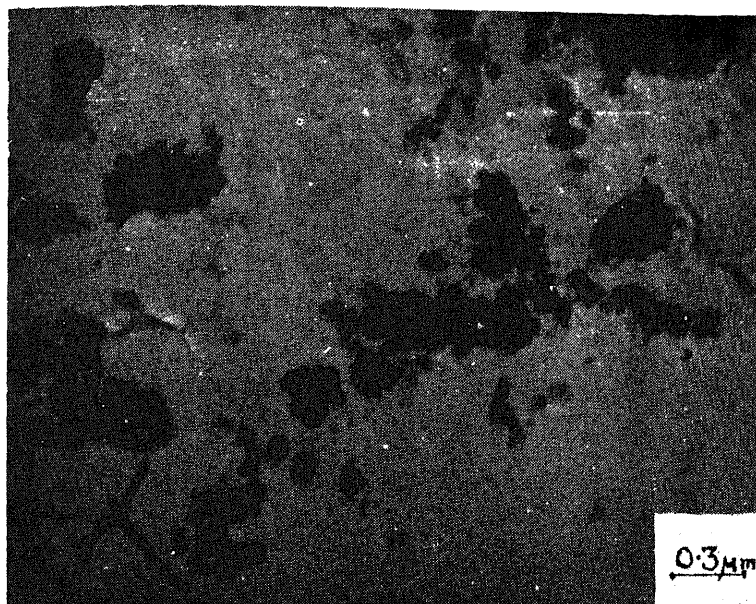


Figure 4. TEM micrographs of NiFe_2O_4 precursor powders, prepared in the absence of urea, after calcination at 450°C for 4 h.

of it. This homogenizes the bed temperature and local sintering of the powder is avoided and formation of fine particles occur.

4. Conclusion

The PVA added metal nitrate solution evaporation method, in presence/absence of urea, is technically simpler, cost effective, and more time- and energy-efficient than the other reported chemical method for the preparation of fine single phase mixed-oxide powders. The route can be applied for the preparation of a variety of mixed-oxide systems at relatively low external temperatures.

Another major advantage of the route is that the PVA easily decomposes exothermally at 500°C , leaving behind very little carbon residue.

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Combustion synthesis of oxide materials for nuclear waste immobilization

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Abstract. Oxide materials like perovskite, zirconolite, hollandite, pyrochlore, NASICON and sphene which are used for nuclear waste immobilization have been prepared by a solution combustion process. The process involves the combustion of stoichiometric amount of corresponding metal nitrates and carbonylhydrazide/tetraformyl trisazine/diformyl hydrazide at 450°C. The combustion products have been characterized using powder X-ray diffraction, infrared spectroscopy, and ^{29}Si MAS-NMR. The fine particle nature of the combustion derived powders has been studied using density, particle size, BET surface area measurements and scanning electron microscopy. Sintering of combustion derived powder yields 85–95% dense ceramics in the temperature range 1000°–1300°C.

Keywords. Combustion synthesis; SYNROC; nuclear waste immobilization.

Introduction

Ceramic oxide materials such as perovskite (CaTiO_3), zirconolite $\text{CaZrTi}_2\text{O}_7$, hollandite $\text{Ba}_{1-23}\text{Al}_{2-46}\text{Ti}_{5-54}\text{O}_{16}$, pyrochlore ($\text{Ln}_2\text{Zr}_2\text{O}_7$ and $\text{Ln}_2\text{Ti}_2\text{O}_7$, Ln = rare earth metals), NASICON ($\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$) and sphene (CaTiSiO_5) have gained tremendous interest because of their application as the geological medium for the immobilization of radioactive wastes (Clarke 1983; Hayward and Cecchetto 1984). The stacking of the metal-oxygen polyhedra in their structure results in the formation of cavities and vacant interlayers capable of accommodating a large number of radioactive ions. The most popular procedure employed by the nuclear power establishments during the past few decades has been to incorporate the nuclear wastes into silicate glasses. The serious disadvantage recognized recently is that the silicate glasses readily devitrify when subjected to action of water and steam at elevated temperatures and pressure (MacCarthy *et al* 1978). Therefore an alternative method using ceramic materials in which the radionuclides are incorporated into solid solution in an assemblage of mineralogical phases is adopted by several workers (MacCarthy and Davidson 1975; Ringwood *et al* 1979). Since the nuclear waste contains a variety of ions of various sizes and charge, it is difficult to incorporate all the radioactive ions in one phase. So a mixture of phases, i.e. a phase assemblage in which the phases are chemically compatible with one another, has been considered. A variety of phase assemblages have been proposed like hypercalcine (MacCarthy 1976; 1979) containing scheelite, cubic zirconia, spinel, rutile, corundum and pollucite phases. Synthetic rock (SYNROC), a titanate based ceramic containing hollandite, perovskite and zirconolite phases, has been investigated (Ringwood *et al* 1979) for nuclear waste immobilization. Fine crystals of sphene (CaTiSiO_5 , calcium titanate) in an aluminosilicate glass matrix are also being

studied as alternatives to glasses for the immobilization of nuclear wastes (Hayward and Cecchetto 1984; Hayward *et al* 1984).

The nuclear applications need highly reactive oxide powders in order to readily assimilate the radioactive nuclei in their structure. The conventional methods (heat and beat, shake and bake) of preparing these materials involve firing the component oxides at elevated temperature with repeated grinding operations to ensure homogeneity. However wet chemical methods (Segal 1989) like sol-gel which have better control over homogeneity, stoichiometry and purity are increasingly used these days for the preparation of sinterable powders. In this paper, we describe the preparation of perovskite (CaTiO_3), zirconolite ($\text{CaZrTi}_2\text{O}_7$), hollandite ($\text{Ba}_{1.23}\text{Al}_{2.46}\text{Ti}_{5.54}\text{O}_{16}$) and sphene (CaTiSiO_5) by solution combustion method. The combustion derived powders have been characterized by powder pattern X-ray diffractometry, IR spectroscopy, BET surface area analysis, particle size measurement, ^{29}Si MAS-NMR, density measurements and scanning electron microscopy.

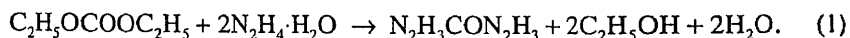
2. Experimental

2.1 Preparation of titanyl nitrate

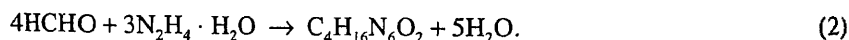
Titanyl nitrate $\text{TiO}(\text{NO}_3)_2$ was prepared by the addition of 1:1 ammonia solution to titanyl chloride, TiOCl_2 at 4°C . The resulting hydroxide product was dried and dissolved in a minimum quantity of dilute HNO_3 to get titanyl nitrate. The formation of titanyl nitrate was confirmed by determining the Ti content gravimetrically as TiO_2 (Yamamura *et al* 1985).

2.2 Preparation of fuels

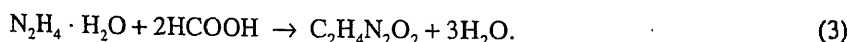
2.2a Preparation of carbohydrazide (CH): Carbohydrazide (CH) $\text{N}_2\text{H}_3\text{CON}_2\text{H}_3$ was prepared as reported (Mohr *et al* 1953) by the hydrazinolysis of diethylcarbonate using hydrazine hydrate (99%)



2.2b Preparation of tetraformyl trisazine (TFTA): Tetraformyl trisazine (TFTA) $\text{C}_4\text{H}_{16}\text{N}_6\text{O}_2$ was prepared by the dropwise addition of 4 mole of formaldehyde to 3 mole of hydrazine hydrate maintaining the temperature below 5°C as reported below (Mashima 1966).



2.2c Preparation of diformyl hydrazide (DFH): $\text{N,N}'$ -diformyl hydrazine (DFH) $\text{C}_2\text{H}_4\text{N}_2\text{O}_2$ was prepared by heating 1:2 molar ratio of hydrazine hydrate and formic acid on a steam bath overnight. The solvent was removed and ethanol was added. The solid separated was collected and dried (Ainsworth and Jones 1955)



3.3 Calculation of stoichiometry for the combustion reactions

The stoichiometric composition of the redox mixtures for the combustion were calculated using the total oxidizing (O) and reducing (F) valencies of the components which serve as the numerical coefficient for the stoichiometric balance, so that the equivalence ratio Φ_e is unity (i.e. O/F = 1) and the energy released by the combustion is maximum (Jain *et al* 1981). Based on the concepts of propellant chemistry the elements C, H, Ca, Ti, Zr, Ba, Al and Si are considered as reducing elements with valencies of 4+, 1+, 2+, 4+, 4+, 2+, 3+ and 4+ respectively and oxygen as an oxidizer having the valency of 2-. The valency of nitrogen is taken as zero because of its conversion to molecular nitrogen during combustion. Accordingly the valencies of $\text{Zr}(\text{NO}_3)_4$, $\text{TiO}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, $\text{CH}_6\text{N}_4\text{O}$ (CH), $\text{C}_4\text{H}_{16}\text{N}_6\text{O}_2$ (TFTA) and $\text{C}_2\text{H}_4\text{N}_2\text{O}_2$ (DFH) will be 20-, 10-, 10-, 10-, 15-, 15+, 28+, 8+, respectively. The valency of SiO_2 is zero.

3.3a Synthesis of calcium titanate: Synthesis of calcium titanate (CaTiO_3) is described as a representative. Calcium nitrate (5 g), titanyl nitrate (4 g) and TFTA (3 g) were dissolved in minimum amount of water in a pyrex dish. The dish containing the solution was introduced into a muffle furnace maintained at 450°C.

Table 1. Composition of the redox mixtures and the thermal phase evolution of combustion products.

Composition	Compound	Calcination Temp. (°C)	Phases
A (5 g) + B (4 g) + TFTA (2.7 g)	CaTiO_3	—	—
A (2 g) + B (3.48 g) + C (3.87 g) + CH (4.76 g)	$\text{CaZrTi}_2\text{O}_7$	As prepared 700 900 1000	TiO_2 (a) + ZrO_2 (t) TiO_2 (r) + ZrO_2 (r) + CaTiO_3 + $\text{CaZrTi}_2\text{O}_7$ TiO_2 (r) + $\text{CaZrTi}_2\text{O}_7$ $\text{CaZrTi}_2\text{O}_7$
D (1 g) + B (3.24 g) + E (2.9 g) + CH (3.7 g)	Hollandite	As prepared 1000	Amorphous Hollandite
A (1.84 g) + B (4.7 g) + C (1.02 g) + D (0.52 g) + E (2.48 g) + CH (2 g) + TFTA (2.1 g)	SYNROC	As prepared 1100	Amorphous + perovskite Perovskite + Zirconolite + Hollandite
A (6.83 g) + B (5.43 g) + F (1.47 g) + CH (6.5 g)	CaTiSiO_5	As prepared 400 600 800 875 950 1200	Amorphous + CaO + TiO_2 (r) CaO + TiO_2 + CaTiO_3 CaTiO_3 + CaO + TiO_2 CaTiSiO_5 + CaTiO_3 + SiO_2 CaTiSiO_5 + CaTiO_3 + SiO_2 CaTiSiO_5 + CaTiO_3 + SiO_2 CaTiSiO_5
A (4.53 g) + B (3.6 g) + F (1.15 g) + TFTA (2.5 g)	CaTiSiO_5	1250	CaTiSiO_5
A (4.84 g) + B (3.85 g) + F (1.23 g) + DFH (9G)	CaTiSiO_5	1200	CaTiSiO_5

A = $\text{Ca}(\text{NO}_3)_2$, B = $\text{TiO}(\text{NO}_3)_2$, C = $\text{Zr}(\text{NO}_3)_4$, D = $\text{Ba}(\text{NO}_3)_2$, E = $\text{Al}(\text{NO}_3)_3$, F = Fumed SiO_2 , CH = carbohydrazide, TFTA = tetraformyl trisazine, DFH = diformyl hydrazide.

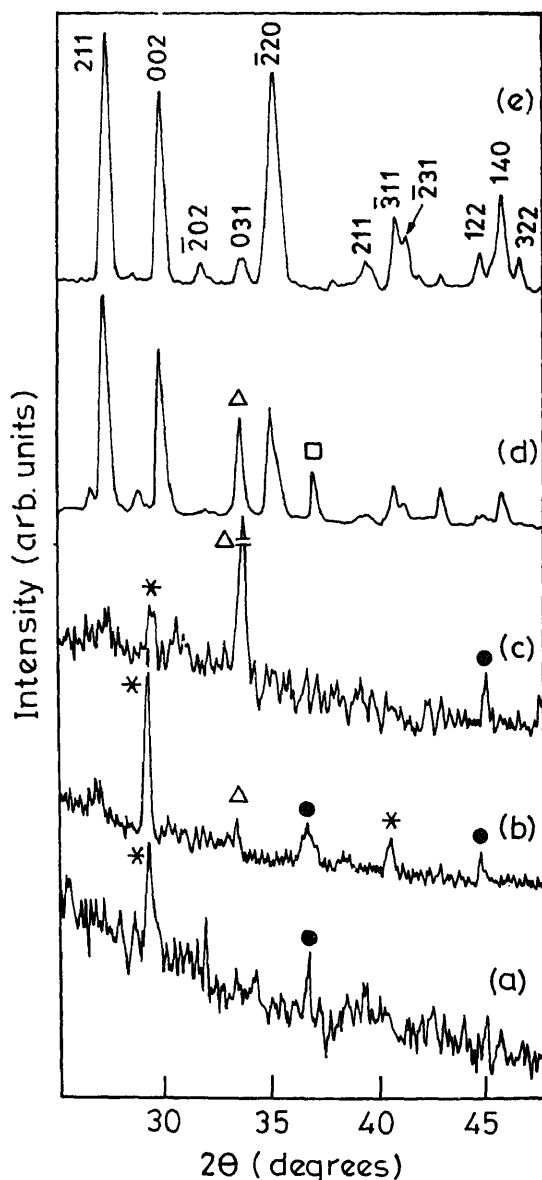


Figure 1. X-ray diffraction patterns of sphene: (a) as prepared, (b) 400°C, (c) 600°C, (d) 875°C and (e) 1200°C. (*, CaO; ●, TiO₂; Δ, CaTiO₃; □, α-crystobalite).

The solution undergoes dehydration followed by decomposition with the evolution of large amount of gases (oxides of nitrogen and ammonia) and ignites to burn with a flame (flame temperature, $900 \pm 50^\circ\text{C}$) yielding voluminous calcium titanate powder in less than 5 min.

Similarly calcium zirconolite, hollandite, SYNROC and sphene (using three different fuels) were prepared using combustion process. Actual compositions of the redox mixture used for the combustion are summarized in table 1.

Table 2. The lattice parameters of the combustion products.

Compound	a (°A)	b (°A)	c (°A)	α (°)	β (°)	γ (°)
CaTiO ₃	5.4138	7.6573	5.3840	90	90	90
CaZrTi ₂ O ₇	12.4412	7.2151	11.50332	90	100.28	90
Hollandite	9.902	9.902	2.865	90	90	90
CaTiSiO ₅ /CH	6.975	8.7175	6.5107	90	113.22	90
CaTiSiO ₅ /TFTA	7.0321	8.7167	6.5508	90	113.69	90
CaTiSiO ₅ /DFH	7.0526	8.6969	6.5612	90	113.93	90

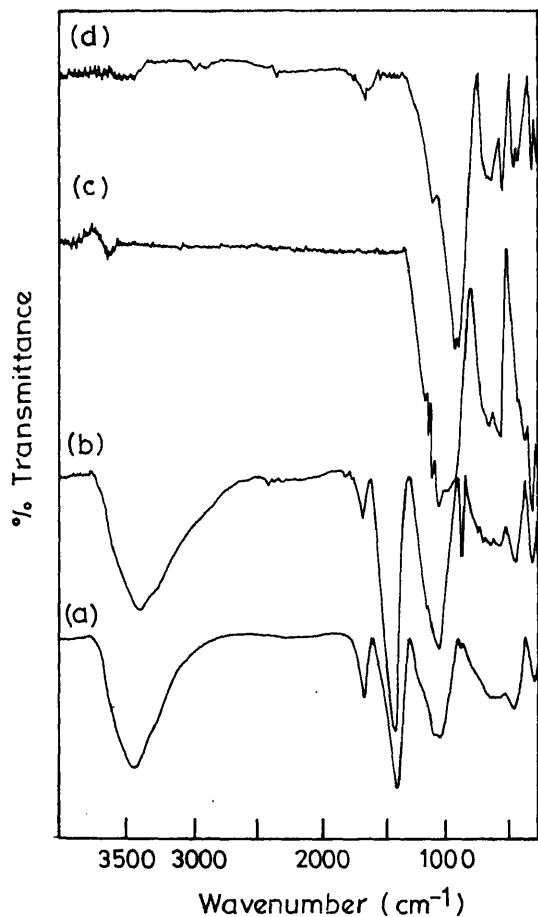


Figure 2. IR spectra of sphene; (a) as prepared, (b) 400°C, (c) 700°C and (d) 1100°C.

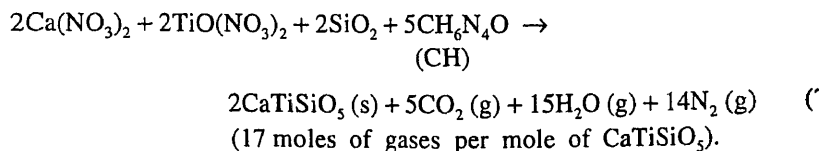
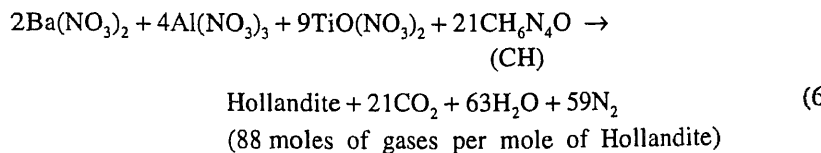
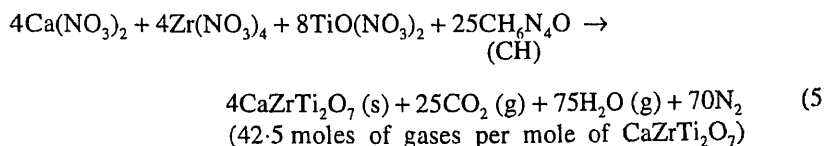
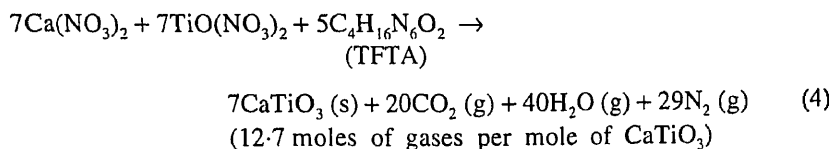
2.3b Product analysis: The combustion derived products have been characterized by powder XRD, recorded using Philips PW 1050/70 X-ray diffractometer with Ni-filtered Cu-K α radiation. Lattice parameters were calculated from XRD pattern in the range of $25^\circ \leq 2\theta \leq 55^\circ$ with a least-squares fit. The IR spectra were

photo sedimentation method (Model SKC 2000 Micron photosizer) was used to determine the agglomerate particle size (i.e., Stokes diameter) and distribution of the particles (histogram). Surface areas were measured using nitrogen gas adsorption multi-point BET method (Model 2100E Accusorb, Micromeritics Instrument Corp., Norcross, GA) assuming a cross sectional area of 0.162 nm^2 for the nitrogen molecule. The powder densities were measured using a pycnometer with xylene as liquid medium.

The combustion derived products were crushed and cold-pressed under 50 MPa uniaxial pressure. The resulting green bodies have 40–50% theoretical density. Sintering of cold-pressed compacts were carried out by heating the specimens at desired temperatures in air. The bulk density of the sintered pellets were measured using Archimedes liquid displacement technique. Microstructure of sintered pellets were studied using a scanning electron microscope (SEM, Model S-150 Stereoscan, Cambridge Physical Sciences, Cambridge, UK).

3. Results and discussion

Formation of calcium titanate, calcium zirconolite, hollandite and calcium titanosilicates by the combustion reactions may be written as:



The solid product of combustion have been identified by their characterist

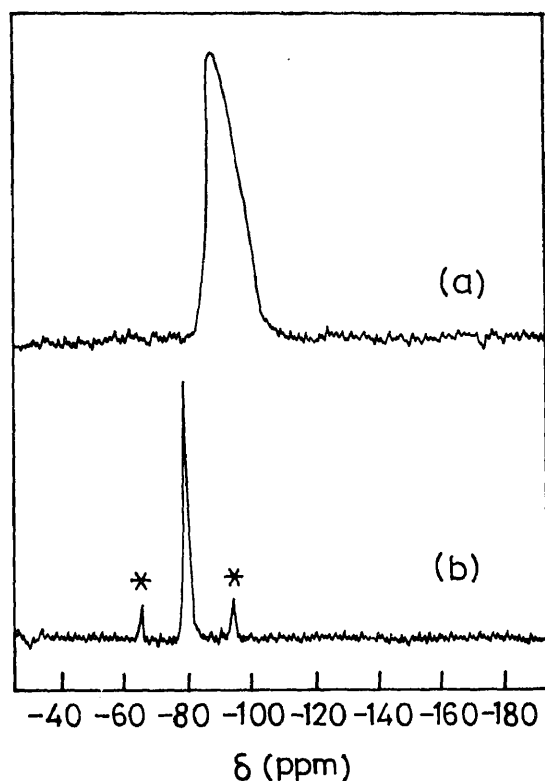


Figure 3. ^{29}Si MAS-NMR of sphene: (a) as prepared and (b) 1100°C .

Table 3. The particulate properties of the combustion products.

Compound	Powder density (g/cm^3)	Surface area (m^2/g)	50% Average agglomerated particle size (μm)	Particle size ^a (μm)	Ref
$\text{Ln}_2\text{Zr}_2\text{O}_7$	4.1	14	1.08	0.10	Arul Dhas and Patil (1993)
NASICONs	2.4–2.8	8–30	6–13	—	Arul Dhas and Patil (1994)
CaTiO_3	3.46	21	0.91	0.08	present study
$\text{CaZrTi}_2\text{O}_7$	2.8	39	9.3	0.05	present study
Hollandite	3.94	37	11.5	0.04	present study
SYNROC	4.98	9	3.6	0.13	present study
Sphene/CH	2.57	67	9.0	0.03	present study
Sphene/TFTA	2.83	65	8.3	0.03	present study
Sphene/DFH	2.9	46	5.7	0.04	present study

^a = calculated from surface area measurement (Irani and Callis 1963).

XRD patterns (JCPDS card: CaTiO_3 ; No. 22-153, $\text{CaZrTi}_2\text{O}_7$; No. 34-167, $\text{Ba}_{1.23}\text{Al}_{2.46}\text{Ti}_{5.54}\text{O}_{16}$; No. 33-133, CaTiSiO_5 ; No. 25-177). Powder XRD patterns of combustion derived sphene (CH process) are shown in figure 1. The as-synthesized residue is X-ray amorphous and shows the presence of weakly crystalline CaO

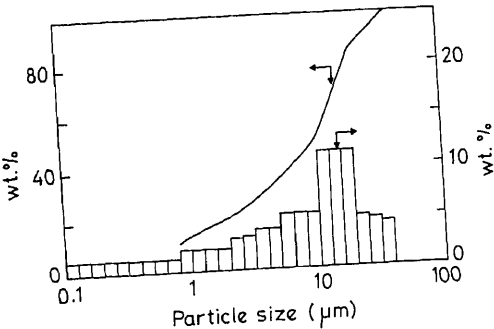
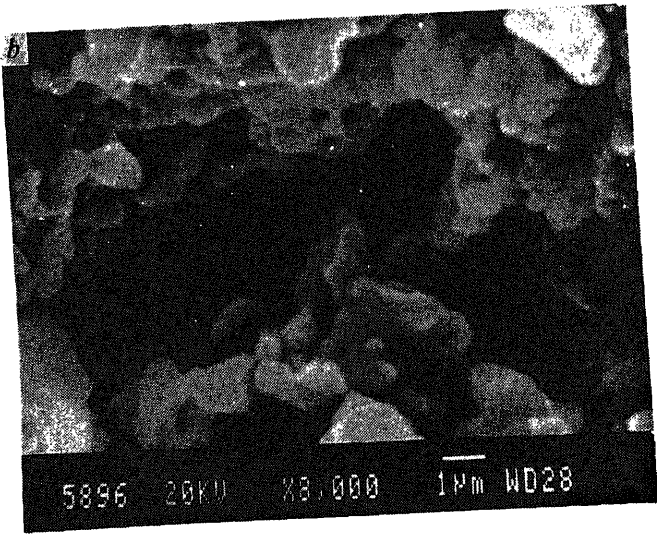
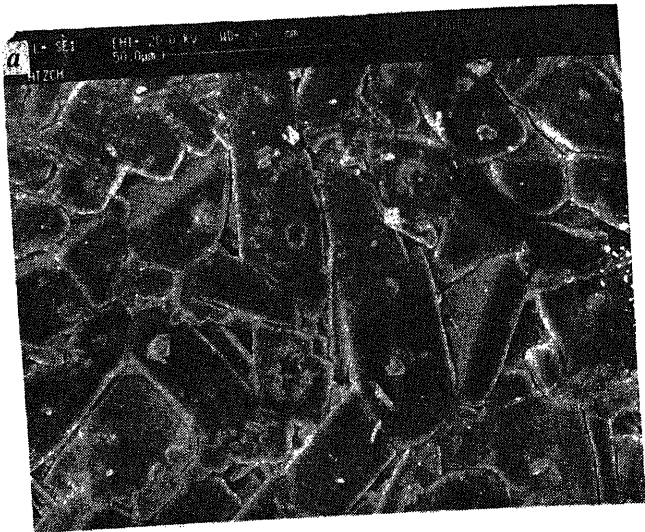


Figure 4. Particle size distribution of combustion derived zirconolite.



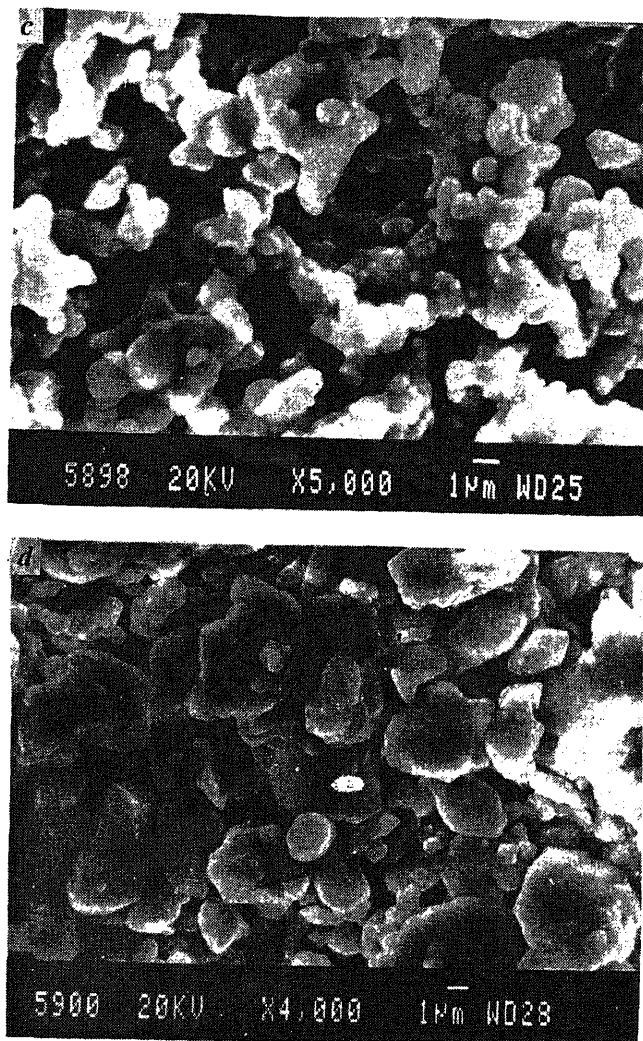


Figure 5. a–d. SEM microstructures; (a) zirconolite sintered at 1250°C, (b) sphene sintered at 1100°C, (c) sphene sintered at 1200°C and (d) sphene sintered at 1300°C.

(figure 1a). At 600°C calcium titanate is the major phase along with CaO and TiO₂ (figure 1c). On further increase in the calcination temperature CaTiO₃, CaO and TiO₂ appear to react with SiO₂ to form CaTiSiO₅. α -cristoballite emerges out as a secondary intermediate phase (figure 1d) between 850°C and 1000°C as reported (Chen *et al* 1994). As the formation of CaTiSiO₅ progresses the amount of CaTiO₃ and SiO₂ decreases. The lattice parameters calculated with a least squares-fit using XRD reflections are given in table 2. These values are in good agreement with those reported in literature.

Various intermediate phases formed during the calcination are summarized in table 1. Powder XRD pattern of as-synthesized zirconolite showed the presence of

TiO₂ (anatase) and tetragonal ZrO₂. At 700°C TiO₂, ZrO₂ and CaTiO₃ phases are observed along with a small amount of zirconolite. On further increase in the calcination temperature CaTiO₃ appears to react with TiO₂ and ZrO₂ to form zirconolite. The formation of single phase zirconolite occurred at 1000°C. The relatively low formation temperature (1000–1200°C) of zirconolite, hollandite and sphene indicates the high reactivity of combustion products.

The IR spectra of combustion derived sphene are shown in figure 2. The IR spectra show the characteristic absorption of SiO₄ tetrahedra at 560 and 880 cm⁻¹ (figure 2d). The absorption band around 675 cm⁻¹ is assigned to TiO₆ octahedra (Chen and Liu 1994). It is noted that the combustion derived sphene shows broad band around 3415 and 1640 cm⁻¹ which corresponds to O–H stretching and bending vibrations and a sharp absorption band around 1380 cm⁻¹ due to NO₃ stretching (figure 2a). The intensities of these three absorption bands decrease gradually on heating the sample to higher temperature. When the sample is heated above 600°C the absorption bands corresponding to the impurities completely disappear (figure 2c). The occurrence of impurities, such as NO₃ and OH in the combustion synthesized sphene could be due to the presence of fumed SiO₂ in the redox mixture which reduces the flame temperature thereby giving undecomposed products.

The ²⁹Si MAS-NMR of as prepared sphene by CH process shows a broad resonance at -110 ppm (figure 3a) and corresponds to amorphous silica (Macial and Sindorf 1980). The ²⁹Si NMR of heat-treated sphene at 1100°C for 1 h shows a sharp resonance at -80 ppm (figure 3b) consistent with SiO₄ tetrahedra (Lippmaa *et al* 1980). This is a low field shift compared with the resonance frequency of pure SiO₂ which confirms the formation of single phase sphene.

The particulate properties of the combustion derived oxide materials used for nuclear waste immobilization are summarized in table 3. The powder densities of the combustion products range from 60–75% of the theoretical value which indicate the porous nature of the combustion residue. The high surface area of the combustion derived products ranges from 8–67 m²/g and this could be attributed to the large amount of gases evolved during combustion [(4)–(7)] which dissipate the heat thereby inhibiting sintering of the combustion products. The 50% average agglomerated particle size of the combustion derived materials ranges from 0.9–13 µm. As a representation the particle size distribution of zirconolite powder is shown in figure 4. It shows that 60% of the particles are distributed between 10 and 13 µm range with the average agglomerated particle size of 9.3 µm.

The SEM microstructure of sintered zirconolite (1250°C) is shown in figure 5a. The SEM micrograph exhibits the presence of dense elongated grains with linear grain boundaries. The grain size vary from 40–50 µm. The microstructural development of sintered sphene compacts (1100°–1300°C) is illustrated in figures 5b–d. The SEM microstructure of sintered body (1100°C) shows poor densification (63% theoretical density) and the presence of platelet particles with large pores and cavities. When the sintering temperature is increased to 1200°C, the sintered body exhibits a network of nearly equiaxial grains with the homogeneous distribution of pores. The sintered (1300°C) sphene compact shows almost pore free state with the irregular shaped grains (figure 5d). The grains are not well connected and the grain size ranges from 1–5 µm. The sintered body achieves more than 85% theoretical density. Sintering of sphene above 1300°C leads to melting of sphene which eventually reduces the sintered density. The lower sintering temperature of combustion

derived zirconolite and sphene could be due to the large surface area and the fine particle nature of the combustion products.

Conclusion

The solution combustion process has been used successfully to prepare reactive oxide materials, which can be used for nuclear waste immobilization. The sintering of sphene and zirconolite compacts in the temperature range of 1250° and 1300°C for 1 h results in a dense body (85–95% theoretical density). SEM of the sintered compacts of sphene showed the presence of almost equiaxial grains of 1–5 µm size and that of zirconolite showed the presence of elongated grains of 40–50 µm size.

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Cd₂SnO₄—its sol-gel preparation and materials properties

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Abstract. Cd₂SnO₄ powder has been synthesized through acrylamide sol-gel route for the first time. The gelation-calcination steps have been studied. Morphological examination of the network matrix and the calcined products has been done through SEM. XRD shows the orthorhombic structure of the Cd₂SnO₄ powder obtained. Arrhenius plots yield activation energies of 0.01 and 0.61 eV for the low and high slope regions, respectively. A semiconductor to metal transition is observed in the range 210–225°C.

Keywords. Cadmium tin oxide; sol-gel; acrylamide.

1. Introduction

Fine semiconductor oxides are important materials on account of their varied applications in sensors (Advani and Gordon 1980), rechargeable batteries (Hashemi *et al* 1988; Jayachandran *et al* 1993) and energy converting and conserving systems (Cardile 1991) to name just a few. Rapid progress has been made in the synthesis of semiconductor oxides through new techniques like the sol-gel method with many advantages over the conventional solid-state route. The sol-gel method enables the production of a wide range of fine particles of controlled size and morphology, high purity, molecular homogeneity and reduced processing temperature.

The currently well-known sol-gel processes (Hench and West 1990) employ the expensive metal-alkoxide precursors. In this report, an inexpensive but efficient organic polymer is used for gel formation. Here, an organic polymer such as polyacrylamide helps in the formation of submicron pores in the gel matrix (Tanaka 1981). Aqueous solutions are gelled by the *in situ* formation of an organic network and the reactions, in the trapped precursor inorganic salt solution, form hydrous oxides or hydroxides of metals. The subsequent direct calcination of the dried gel produces submicron size semiconductor oxide powders.

Cd₂SnO₄ has been synthesized by solid-state reaction (Smith 1960; Golestani-Fard *et al* 1983). For the first time, this compound has been synthesized by the organic sol-gel method by the present authors and a detailed account of the gelation-calcination processes and the materials properties of the synthesized powder is presented here.

2. Experimental

AR grade CdCl₂, SnCl₄, citric acid, acrylamide, N,N'-methylene-bis-acrylamide and ammonium persulphate were used. The gel formation and calcination steps are

explained in a later section. A programmable furnace, Heraeus Model No. K 1710, was used for heating. XRD analysis was carried out with a JEOL JDX 803-a X-ray equipment using CuK_α radiation through a Ni filter. DTA measurements were made with a fabricated set-up consisting of a ceramic furnace which could go up to 1000°C , a chromel-alumel thermocouple, a ceramic sample holder and an X-Y-t recorder. SEM analysis was done using a scanning electron microscope, JSM 35 CF JEOL. Resistance vs temperature was measured by the two-probe method.

3. Results and discussion

The flow chart for the synthesis of Cd_2SnO_4 powder by the sol-gel route is given in figure 1. The precursor was prepared by mixing aqueous chlorides of cadmium and tin in the mole ratio of 2 : 1. Citric acid was used as the complexing agent and to avoid precipitation. Aqueous ammonia was used to adjust the pH at 2, 4, 5, 7 and 10.

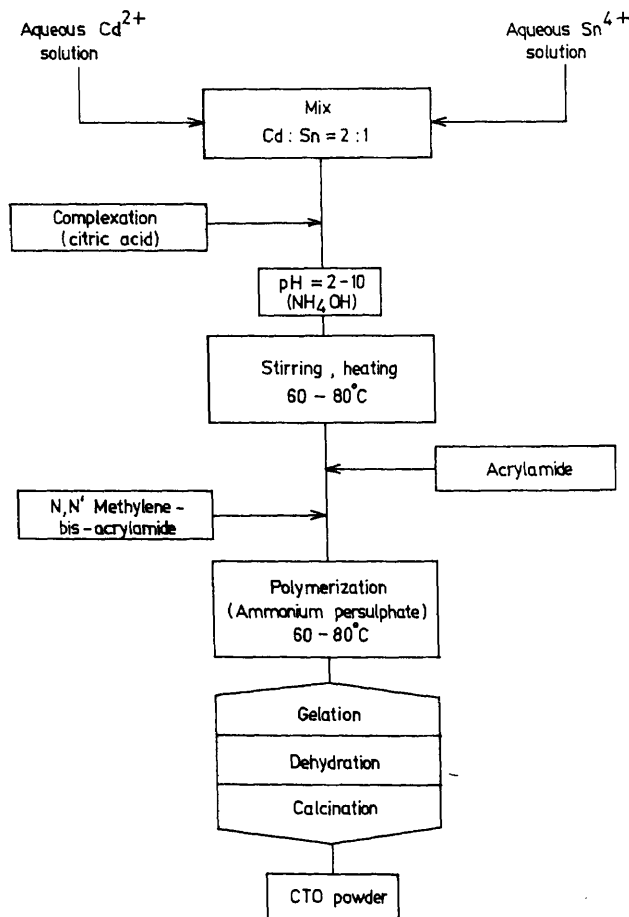


Figure 1. Flow chart of the sol-gel process.

The clear solution was heated to 60–80°C. 6 g of acrylamide and 1 g of N,N'-methylene-bis-acrylamide were added gradually one after the other under continuous stirring and the solution temperature maintained for about 15 min. Then 0.05 g of ammonium persulphate was added as polymerization catalyst. In about 2–5 min gelation was complete and a translucent and non-sticky gel was formed.

Dehydration of the gel should be done carefully under controlled heating steps. If the temperature is lower than 50°C, it takes around a week for complete dehydration. At temperatures greater than 150°C, there is a very large increase in volume, even up to 20 times the initial volume, and the gel turns into a loose dark powdery residue which is undesirable. Dehydration at 100°C for 48 h is found to be optimum for getting a shrunken, white or light yellow coloured residue. The volume reduces to about a tenth of its initial volume due to the removal of the trapped water in the pores.

The thermal behaviour of the dried residue was examined by DTA and is shown in figure 2. The first endothermic peak at about 75°C is ascribed to the evaporation of water physically adsorbed on the gel. The second endothermic peak at about 230°C may be due to the removal of the functional groups (Byong-Ho Kim *et al* 1992) and the decomposition of hydroxides. The two exothermic peaks in the temperature range of 500–600°C might be attributed to the burnout of the carbon. The broad exothermic region from about 700 to 1000°C may be associated with the formation of CdO and SnO_2 and subsequent reaction to form Cd_2SnO_4 as seen from the XRD analyses. The process of Cd_2SnO_4 formation continues up to 900°C. The fall in the curve beyond 900°C may be due to the decomposition of the formed Cd_2SnO_4 into SnO_2 and CdSnO_3 as borne out by the XRD results.

Based on the DTA analysis, calcination was carried out under controlled heating steps. An initial slow heating rate (HR) had to be maintained to break the organic network. Up to 600°C the HR was maintained at 2, 5 and 10°C per min and then calcination was carried out at temperatures of 700, 800, 900 and 1000°C for different durations.

At 2°C per min HR, the reaction was too slow and the product was a powder with distinct black and yellow components. At 5°C per min HR, only yellow

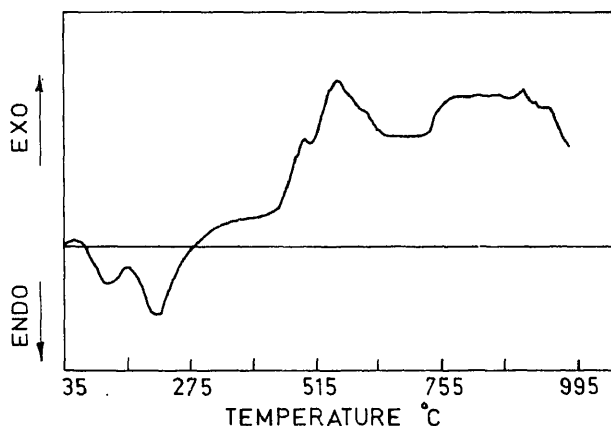


Figure 2. DTA curve of the dried gel residue.

powder resulted after calcination. At 10°C per min HR, a white coloured mass resulted. These observations lead to the conclusion that the optimum HR was 5°C per min to obtain yellow coloured powder after calcination as shown in figure 3a. The typical colour of Cd_2SnO_4 powder was yellow.

Calcination was done at temperatures of 700, 800, 900 and 1000°C for a duration of 3 h. The optimum calcination temperature was found to be 900°C at which, only yellow coloured powder was obtained as shown in figure 3b. At 700 and 800°C, the powder appeared to have both white and yellow components. At 1000°C only white coloured powder resulted. It is presumed that other phases of cadmium tin oxide are formed at temperatures higher than 900°C. The effect of calcination duration was studied by calcining for 1, 3 and 5 h. Pure yellow coloured powder was obtained for a calcination duration of 3 h as shown in figure 3c.

The calcined powders were subjected to XRD analysis. A multiplot of XRD patterns of the dried gels and the calcined products obtained at different temperatures in air is shown in figure 4. The dried gel is amorphous. Sharp XRD peaks are noticed for the powders obtained at all the calcining temperatures, which show that crystallization is there even at 700°C, the lowest temperature of calcination.

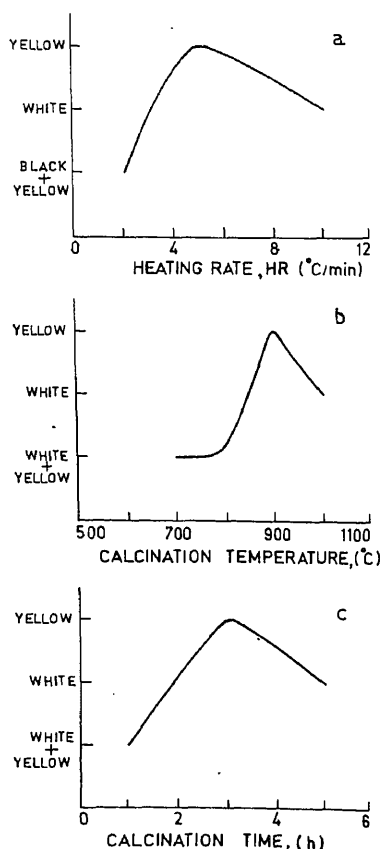


Figure 3. Colour changes of the calcined product under different preparative parameters of (a) heating rate (HR), (b) calcination temperature and (c) calcination time.

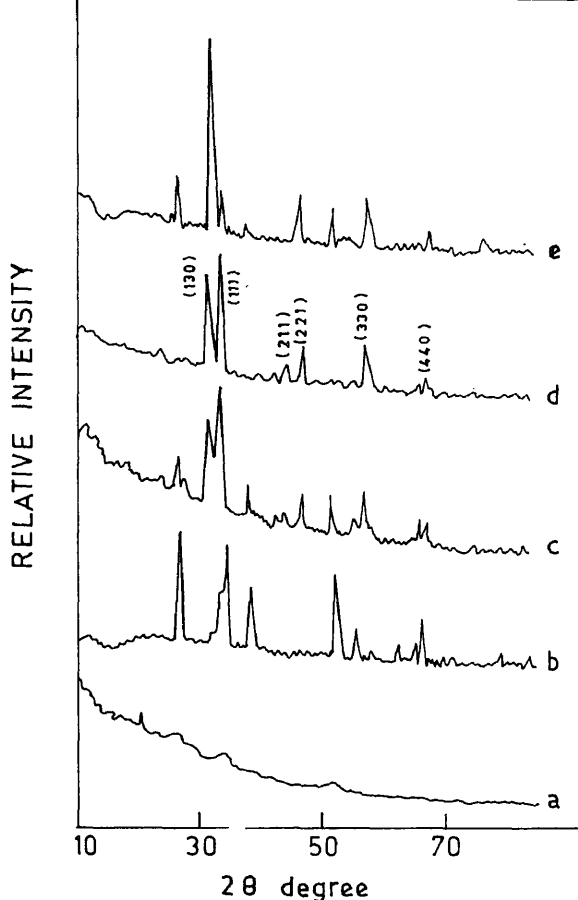


Figure 4. XRD patterns of (a) dried gel, (b) calcined at 700°C, (c) calcined at 800°C, (d) calcined at 900°C and (e) calcined at 1000°C.

On the basis of the XRD analyses, a synthesis mechanism of Cd_2SnO_4 powder can be proposed as given in table 1.

The Cd-Sn hydroxide gel first decomposes leading to the formation of CdO and SnO_2 . As the temperature increases CdO reacts with SnO_2 leading to a gradual formation of Cd_2SnO_4 till all CdO is used at 900°C. The product assumes a yellow colour completely indicating the completion of the formation of Cd_2SnO_4 phase. However, the Cd_2SnO_4 obtained contains a little amount of SnO_2 as a secondary phase. When the calcination temperature reaches 1000°C, Cd_2SnO_4 reacts with the residual SnO_2 and disintegrates to produce CdSnO_3 and SnO_2 as the predominant phases together with some Cd_2SnO_4 .

These results are somewhat contrary to earlier observations (Golestani-Fard *et al* 1983) for Cd_2SnO_4 formation by the solid state reaction of 2:1 CdO and SnO_2 . They observed Cd_2SnO_4 phase at 1050°C and at higher temperatures, it decomposed to CdO and CdSnO_3 phases. The absence of CdO in the sol-gel derived Cd_2SnO_4 powders calcined at above 900°C for prolonged duration was due to the fact that CdO sublimation in dynamic air began at about 900°C (Cardile 1991).

Calcination temperature (°C)	Chemical reaction	Phases observed in XRD pattern
700	$\text{Cd}(\text{OH})_2 \rightarrow \text{CdO} + \text{H}_2\text{O}$ $\text{SnO}_2 \cdot x\text{H}_2\text{O} \rightarrow \text{SnO}_2 + x\text{H}_2\text{O}$	CdO SnO ₂
800	$\text{CdO} + \text{SnO}_2 \rightarrow \text{Cd}_2\text{SnO}_4 + (\text{SnO}_2) + (\text{CdO})$	CdO SnO ₂ Cd ₂ SnO ₄
900	$\text{CdO} + \text{SnO}_2 + \text{Cd}_2\text{SnO}_4 \rightarrow \text{Cd}_2\text{SnO}_4 + (\text{SnO}_2)$	Cd ₂ SnO ₄ SnO ₂
1000	$\text{Cd}_2\text{SnO}_4 + \text{SnO}_2 \rightarrow \text{CdSnO}_3 + (\text{SnO}_2) + (\text{Cd}_2\text{SnO}_4)$	CdSnO ₃ SnO ₂ Cd ₂ SnO ₄

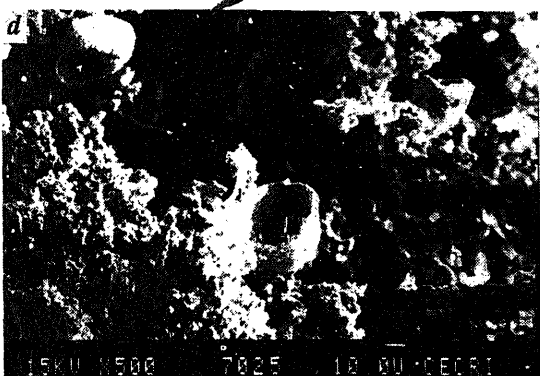
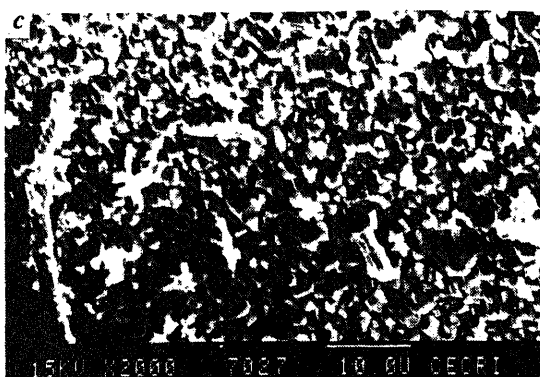
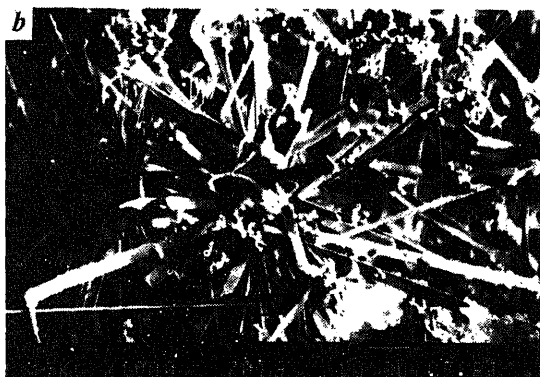
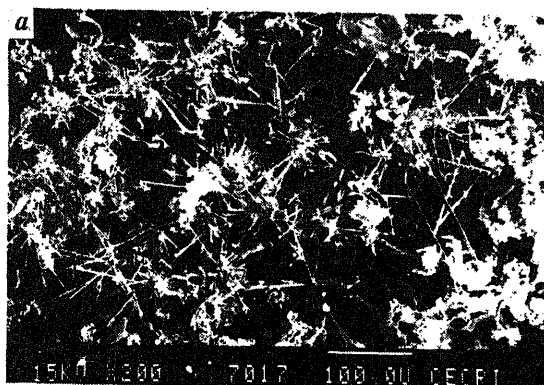
Morphology of the calcined residue and the crushed powder was studied by SEM. The acrylamide sol-gel matrix was a polymeric network with pores of about 1–5 μm diameter (Tanaka 1981). The sol containing the precursors, was trapped in the pores. When dehydration and calcination were carried out, the polymer network evaporated leaving the oxide powder in the form of a loosely held network. This network structure is shown in figure 5a. It is interesting to note that cob-web like formations scattered all over the mass. These structures were interconnected with needles with a diameter of about 1 μm . Figure 5b provides a closer view of an individual cob-web structure. The branches from the centre of the clusters extend to the neighbouring clusters which is the characteristic feature of the acrylamide gel with interconnected pores.

Figure 5c depicts the SEM picture of ground Cd₂SnO₄ powder. It shows an agglomerated mass of grain size about 2 μm . The product obtained at 1000°C shows a different morphology with some cup-like structures made up of fine particles as shown in figure 5d.

The synthesized powder was orthorhombic with lattice parameters $a = 5.560 \text{ \AA}$, $b = 9.894 \text{ \AA}$ and $c = 3.218 \text{ \AA}$ and these compare well with the reported values of $a = 5.563 \text{ \AA}$, $b = 9.892 \text{ \AA}$ and $c = 3.192 \text{ \AA}$ (Bowden and Cardile 1990).

The powder exhibits *n*-type behaviour as observed by the hot-probe method. The log *R* vs temperature variation for the powders prepared at pH 2, 4, 5, 7 and 10 is shown in figure 6. All the curves show a variation in slope in the temperature region of 85–105°C which is in accordance with the reported transition temperature of 84°C for the screen printed Cd₂SnO₄ layer with orthorhombic structure (Setty 1989). The resistance goes on decreasing up to a point and then increases. This continuous decrease in resistance can be ascribed to an increase in the number of electrons which can be attributed to the release of chemisorbed and bound oxygen

Figure 5. Scanning electron micrographs of the (a) uncrumbled network, (b) closer view of an individual cob-web structure, (c) agglomerated mass and (d) powder calcined at 1000°C.



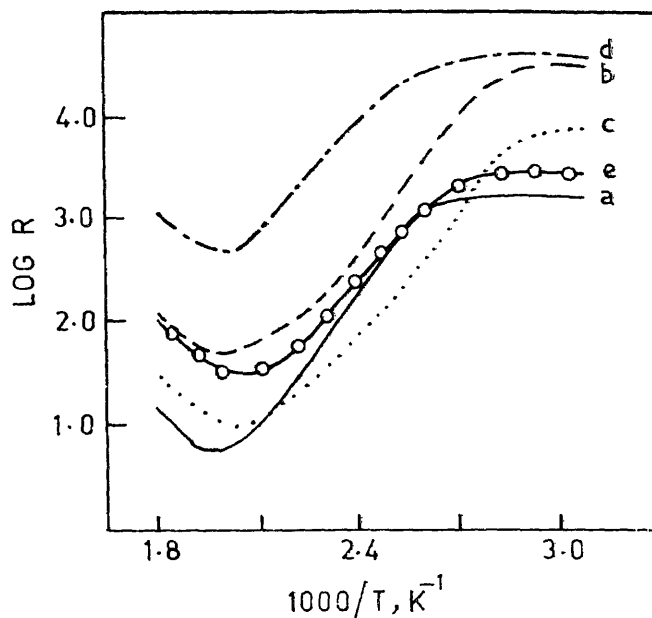
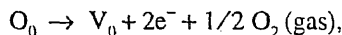


Figure 6. Plot of $\log R$ vs $1000/T$ for powders prepared at (a) pH 2, (b) pH 4, (c) pH 5, (d) pH 7 and (e) pH 10.

Table 2. The optimized process parameters for the synthesis of Cd_2SnO_4 powder by acrylamide for sol-gel method (5 g batches).

Sol pH	5
Gelation temperature	60–80°C
Gelation time	2–5 min
Dehydration temperature	100°C
Dehydration time	48 h
Heating rate	5°C/min
Calcination temperature	900°C
Calcination time	3 h
Colour of the powder	Yellow

species on heating the powder. This process contributes more electrons by the desorption process



resulting in enhanced conduction.

Beyond this point, there is an increase in resistance. The continuous supply of electrons reaches saturation imparting a metal like behaviour to the Cd_2SnO_4 powder. This semiconductor to metal-like transition is observed in the range 210–228°C which is comparable to the range 215–227°C reported earlier (Setty 1989). The calculated activation energy values corresponding to the low and high slope regions are about 0.01 and 0.61 eV respectively which are again comparable to the reported values of 0.01 and 0.76 eV (Setty and Sinha 1986; Setty 1989).

4. Conclusions

A detailed investigation of the synthesis of Cd_2SnO_4 powder through the acrylamide sol-gel route has been presented. It has been possible to synthesize Cd_2SnO_4 powder at a lower temperature of 900°C by this sol-gel route. The optimized process parameters to obtain orthorhombic Cd_2SnO_4 powder are given in table 2. A small amount of SnO_2 is present in the product. The synthesized powder is composed of particles with a narrow size distribution of $1\text{--}3\text{ }\mu\text{m}$. The particles appear to be agglomerated. The product exhibits n -type conductivity and shows a semiconductor to metal transition around $210\text{--}225^\circ\text{C}$, which property makes it useful for thermal switching applications.

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Role of dopant cations in the gelation behaviour of silica sols

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Abstract. Gelation times of tetraethyl orthosilicate-derived sols containing selected di- to tetravalent cations as dopants were noted at different temperatures (15°–50°C). An analysis of these data, in conjunction with relevant published information, led to the tentative conclusions that (i) unhydrolyzed cations in bare form linked negatively charged silicate polymers in sols, thereby accelerating gelation and (ii) hydrolyzed cations retarded the process by offering molecular size-related hindrance and competition for the available water for hydrolysis.

Keywords. Silica sol; sol-gel transition; dopant cations.

1. Introduction

The phenomenon of gelation of silica sols in presence of dopant cations has been attracting the attention of researchers from the early part of this century (Dienert and Wandenbulcke 1924; Hurd *et al* 1958) till date (Bansal 1990; Patra and Ganguli 1992a,b). The common approach followed in most of these investigations was to find out if and how the process of aggregation of silicate species in a sol (reflected by, among others, the gelation time) was accelerated or retarded by a dopant cation. The issue has gained importance in recent times because of the current interest in doped silica gel-glass optics (e.g. Moreshead *et al* 1990; Thomas *et al* 1992), special glasses (Aizawa *et al* 1994) and silicate catalysts (e.g. Lopez *et al* 1991) including zeolite precursors (McCormick *et al* 1987, 1989) of tailor-made specifications, and the expected influence of the dopants on the gel structures (Ganguli 1988; Murakata *et al* 1992). Gelation time is also an indicator of the workability of a sol and therefore, is of great practical significance in sol-gel processing.

Effects of various cations on the gelation behaviour of alkali silicate or alkoxide-derived sols have been studied (discussed in detail later). However, no general picture of the effect seems to have emerged. In addition, parallel investigations have sometimes led to conflicting conclusions, demanding further study. The present work attempts to re-examine the above phenomenon in the light of existing data and new information on gelation (used as a broad term to include condensation and aggregation of polymeric units) of alkoxide-derived silica sols in presence of selected di- to tetravalent cations.

2. Experimental

All the sols were prepared at 25°–27°C from alcohol-free (initially) alkoxide-water-acid systems. Tetraethyl orthosilicate (TEOS) of purum grade was used as the source of silica with H₂O : TEOS : H⁺ molar ratio at 14 : 1 : 0.01. Cations in required proportions were added via inorganic compounds (Pb-, Zn- and La-nitrates, ammonium

ceric nitrate, Al-chloride, Zr-oxychloride and boric acid) dissolved in deionized water. HNO_3 (for nitrates) or HCl (for other compounds) was used as catalyst. The temperature of the hazy two-phase system thus obtained increased to $70^\circ\text{--}80^\circ\text{C}$ with formation of a clear sol, but came back to ambient conditions within about 15 min. The pH was adjusted to 3.5 by addition of dilute NH_4OH solution. All the chemicals were of AR or equivalent grade.

Sol-gel transition was studied at different temperatures ($15^\circ\text{--}50^\circ\text{C}$) in a constant temperature bath ($\pm 1^\circ\text{C}$). Sols of 15 ml volume in closed containers were used. Gelation times at 25°C and higher temperatures were repeated for check under similar conditions; the differences were found to be reasonably small for the present purpose. However, mean values (2–3 experiments) were used in this work.

3. Results

Tables 1–5 present information on the gelling time of silica sols doped with B^{3+} , Al^{3+} , La^{3+} , Zr^{4+} and Ce^{4+} at different temperatures. Similar data for Pb^{2+} and Zn^{2+} have been reported earlier (Patra and Ganguli 1992a,b) and will not be presented here in full. The data for 40°C (not given in tables 1–5) for all the seven cations have been pictorially presented in figure 1 for a ready comparison of relative trends of gelation. Note that all the sols were cast at a final pH of 3.5, requiring similar additions of NH_4OH ; the effect of NH_4^+ has therefore been considered to be similar in all cases.

4. Discussion

4.1 Earlier observations on gelation of doped silica sols

The earliest experiments (e.g. Hurd *et al* 1958) on gelation, coagulation or aggregation

Table 1. Gelling times of boron-doped silica sols.

Equivalent mol% B_2O_3	Gelling time (h)			
	15°C	25°C	30°C	50°C
0.5	27.38	8.91	4.95	0.55
1.5	33.08	9.38	5.16	0.58
2.5	40.00	10.83	7.08	1.00
5.0	45.00	15.58	8.33	1.13

Table 2. Gelling times of aluminium-doped silica sols.

Equivalent mol% Al_2O_3	Gelling time (h)		
	15°C	30°C	50°C
0.2	22.00	5.33	0.75
0.5	39.81	7.00	1.08
1.0	92.00	13.75	2.17

Table 3. Gelling times of lanthanum-doped silica sols.

Equivalent mol% La ₂ O ₃	Gelling time (h)		
	15°C	25°C	50°C
0.5	18.62	4.57	0.45
1.0	12.30	3.16	0.35
3.0	6.30	1.99	0.29
5.0	3.01	0.80	0.17

Table 4. Gelling times of zirconium-doped silica sols.

Equivalent mol% ZrO ₂	Gelling time (h)		
	15°C	25°C	50°C
0.5	26.92	10.59	1.99
1.0	47.86	17.58	1.83
3.0	63.00	21.88	1.92
5.0	5.50	3.02	0.78

Table 5. Gelling times of tetravalent cerium-doped silica sols.

Equivalent mol% CeO ₂	Gelling time (h)		
	15°C	30°C	50°C
1.0	23.00	5.89	1.12
3.0	19.49	5.25	0.92
5.0	15.14	4.07	0.80

(taken to be synonymous here) in silica sols as a function of the type of electrolyte present in the system showed monovalent cations to accelerate the process in the order $K^+ > NH_4^+ > Na^+ > Li^+$ at pH = 4.8. Recent work of Bansal (1990) confirmed the accelerating action of Li^+ and Na^+ ; a similar behaviour was also noted for all the alkali cations and tetramethyl ammonium, $(CH_3)_4N^+$ (Wijnen *et al* 1993) by measuring fractal aggregate size as a function of time at pH = 4.0.

Among the divalent ions, Mg^{2+} , Ca^{2+} , Sr^{2+} , Pb^{2+} and Zn^{2+} have been shown to accelerate gelation (Bansal 1990; Patra and Ganguli 1992a,b) at pH values ranging between 3.5 and 4.3. Wijnen *et al* (1993), on the other hand, found the initial silicate aggregate growth to be very slow in presence of Mg^{2+} at pH = 4.0 and considered it to be a retarding process. Divalent copper was shown by Bansal (1990) to retard gelation.

Al^{3+} , Y^{3+} and La^{3+} have been reported to hinder gelation (Bansal 1990); boron is known to behave similarly (Woignier *et al* 1984), though no detailed information is on print. Large amounts (10–50 wt%) of ZrO_2 in SiO_2 sols have been shown to increase the gelling time drastically (Klein 1987).

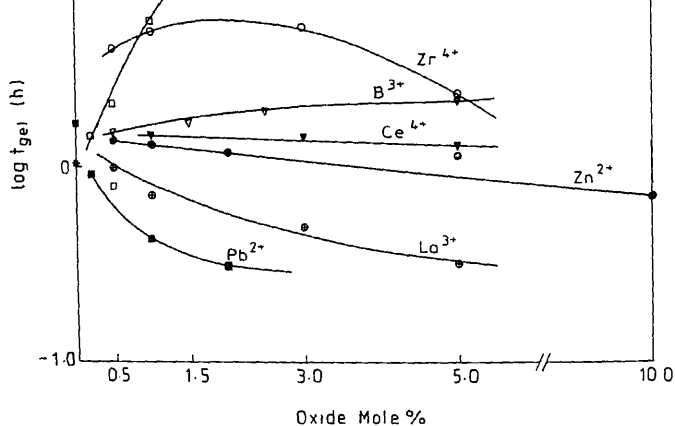


Figure 1. Gelation times at 40°C of some bi- to tetravalent cation doped silica sols (derived from TEOS) prepared at a final sol pH of 3.5. The curves are only visual aids, and do not have any other significance. The asterisk on the Y-axis indicates the gelling time of a pure silica sol catalyzed with HCl; the filled box on the Y-axis indicates the same, catalyzed with HNO₃.

4.2 The past and present results and their interpretation

A comparison of the results presented in tables 1–5 and figure 1 with the published information assembled in §4.1 gives a first hand indication of a general trend of the role of cations in the gelation of a silica sol: (i) Monovalent ions in general accelerate gelation; (ii) divalent ions mostly accelerate gelation (except Cu²⁺); and (iii) small trivalent and tetravalent ions hinder gelation, and ions with radius ~ 1 Å may do so under suitable conditions.

Under the conditions of this work (i.e. alcohol-free solution) the first major interaction of the cations would be with water molecules, i.e. *hydration or hydrolysis*. Even when alcohol was present in the original solution, monovalent cations have been shown to be solvated by water rather than ethanol (Sanchez and McCormick 1991). This indicates a clear relationship between hydrated dopant cations and quick gelation. Considering the fact that cations with small size and high formal charge hydrolyze easily in aqueous solutions of suitable pH (Baes and Messmer 1976; Ramsay 1994), it was thought proper to examine the present data in this light.

Figure 2, re-assembled from Baes and Messmer (1976), indicates that at pH = 3.5, cations which clearly accelerated gelation in this work, i.e. Pb²⁺, Zn²⁺, La³⁺ also remained predominantly hydrated; B³⁺ and Zr⁴⁺ which hindered gelation (except for 5 mol% ZrO₂) were hydrolyzed. Boron always remains hydrolyzed in aqueous solution and the reaction steps indicated by Irwin *et al* (1987) clearly show how it hinders hydrolysis-condensation of Si-alkoxy group. Zirconium forms a cyclic tetramer, [Zr₄(OH)₈(H₂O)₈]⁸⁺ in oxychloride solutions (Clearfield and Vaughan 1956). Al³⁺ also hindered gelation, though figure 2 is not clear about its hydrolyzability at pH = 3.5. Recently, Klopogge *et al* (1993) used NMR data to show that AlOH²⁺ started

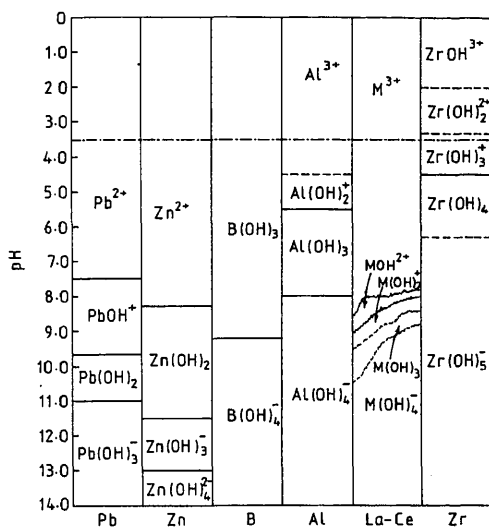


Figure 2. Predominance diagrams for hydration/hydrolysis of cations related to the present work in aqueous solutions of different pH values. Reassembled from Baes and Messmer (1976).

forming at pH 3–3.7 in $AlCl_3$ or $Al(NO_3)_3$ solutions. Bottero *et al* (1982) identified $Al_2(OH)_2^{4+}$ species at pH 3 at the expense of at least 10% of monomers. A rise in temperature during sol preparation (see §2) can be of assistance in the formation of larger polynuclear species. This is also valid for boron and zirconium.

Tetravalent cerium is expected to take part in complexation in most low-pH aqueous solutions. However, it is also a strong oxidizing agent and can be reduced, at least in part, by water (Moeller 1973; Greenwood and Earnshaw 1984) or species present in aqueous solutions to form hydrated (at pH = 3.5) Ce^{3+} , promoting gelation in silica sols.

Sanchez and McCormick (1991) suggested formation of ion-pair complexes between alkali cations and negatively charged silicate groups in TEOS sols to explain enhanced condensation. Patra and Ganguli (1992a) suggested formation of transition state bonds between O^- (of silicate polymers) and M^{2+} cations to accelerate gelation. In both cases, facile shedding of hydration shells (thinner for larger ions) has been assumed. This generalized approach has been found to fit satisfactorily in most cases of relatively quick gelation of cation-doped silica sols.

A simple correlation between a hydrolyzed dopant cation and retardation of gelation of a silica sol seems difficult because of the wide differences among the nature and products of hydrolysis (and eventually, polymerization) of different cations under a given set of experimental conditions (e.g. solution pH, temperature, water/cation ratio). It is, however, noted that even the smallest product of hydrolysis of a cation is sufficiently larger than the corresponding bare cation, and due to this enhanced size, can offer geometrical hindrance to small silicate polymers in approaching each other; this is expected to retard their already slow rate of condensation (shown by the very slow increase in viscosity of TEOS-derived sols). Another factor involved in this process is the competition between silicon and the dopant cation for the available water for hydrolysis; this is also known to retard the hydrolysis of TEOS (Boilot *et al* 1988; Patra 1992; Fukui *et al* 1992).

5. Conclusion

Based on the previous and present information, it can probably be commented that broadly speaking (i) a hydrated cation assists gelation of a silica sol by shedding the hydration shell and cross-linking silicate polymers; and (ii) a hydrolyzed cation hinders gelation by growing in molecular size and offering size-related hindrance in the cross-linking process. This has direct bearing on predicting and manipulating the workability of a sol (i.e. time available for casting, coating etc before gelation) and thus, is of significant practical utility.

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Interfacial mechanisms controlling phase formation in sol-gel derived lead zirconate titanate thin films

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Abstract. An RBS study has been carried out to study the relative extent of Pb diffusion in the substrate from PZT films. It is found that extensive diffusion of Pb occurs into the quartz substrate making the film severely deficient in Pb. No such diffusion occurs in the case of PZT films on sapphire and the concentration of Pb is near stoichiometric, except for a small loss due to volatilization. Excessive Pb deficiency, rather than any epitaxial effect, has earlier been proposed by us to be the crucial factor responsible for the existence of the pyrochlore phase in PZT thin films on substrates such as Si, glass, quartz etc. The present results confirm this. The effects of other process variables such as thickness and chemical composition (Zr/Ti ratio) of the film can also be understood in terms of the same phenomenon.

Keywords. PZT; phase formation; sol-gel; thin film.

1. Introduction

Ferroelectric materials display a variety of phenomena which include ferroelectricity (spontaneous electric polarization which can be reversed by an electric field), pyroelectricity (change in electric polarization due to a change in temperature), piezoelectricity (generation of electric charge by application of mechanical pressure or, conversely, production of mechanical strain by application of electric field), high dielectric constant and electro-optic behaviour. This makes these materials useful in a variety of applications (table 1). In the bulk form barium titanate (BaTiO_3) and lead zirconate titanate (PZT) have long been used as capacitors and piezoelectric elements respectively. In the thin film form also they have numerous present and potential applications. Some of these are shown for PZT in table 2. Thin films of lead zirconate titanate (PZT), chemically represented by $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, are currently being studied with increasing interest because of their potential use in piezoelectric, pyroelectric, electro-optic devices and non-volatile memory applications. Phase diagram for PZT is represented as a binary system between lead zirconate (PZ) and lead titanate (PT) (figure 1). In this system a morphotropic phase boundary (MPB) exists between the tetragonal and rhombohedral phases at $x = 0.535$. The compositions near the MPB are of great technological importance because of pronounced maxima in certain properties.

For all applications of PZT, it is desirable to have the material in the ferroelectric perovskite phase, which is readily obtained in bulk and powder form. The as deposited films are usually amorphous and need to be annealed at 500–700°C to form the perovskite phase. However, a pyrochlore phase which is cubic and is not

Table 1. Ferroelectric materials—phenomena and applications.

Phenomena	Applications
Dielectric	Capacitors, sensor, phase shifter
Ferroelectric	Non volatile memory
Pyroelectric	Pyrodetector
Piezoelectric	Acoustic transducer, sensor, SAW device, actuator
Electro-optic	Wave guide, optical memory, display modulator

Table 2. Thin film ferroelectric materials and application.

Material	Phenomena	Applications
Pb(Zr, Ti)O ₃ (PZT)	Dielectric	Non volatile memory
	Pyroelectric	Pyrodetector
	Piezoelectric	SAW substrate
	Electro-optic	Wave guide device
(Pb, La) (Zr, Ti)O ₃ (PLZT)	Pyroelectric	Pyrodetector
	Electro-optic	Wave guide device
		optical memory, SHG display

ferroelectric, first forms at low temperatures (400–550°C) and often does not transform to the perovskite phase at higher temperatures. Thus the film after heat treatment has either the pyrochlore or the perovskite structure. Table 3 summarizes the data from literature. It is seen that factors such as nature of the substrate, thickness of the film, heat treatment conditions etc all influence the phase of the film. In a systematic work carried in our laboratory (Majumder *et al* 1994), films on sapphire, alumina, NaCl and Pt formed a perovskite phase while on quartz, glass and Si the pyrochlore phase was obtained. It was also found that the perovskite structure formed more easily if the film thickness was increased, or if Zr/Ti ratio was decreased or if excess Pb was present.

The initial formation of the pyrochlore phase in thin PZT film has been attributed by us to the presence of a tensile stress in the film in the early stages of heat treatment (Majumder *et al* 1994). The strain energy considerations favour the formation of the pyrochlore phase which is 6.62% less dense than the perovskite phase. The subsequent pyrochlore to perovskite transformation depends as mentioned earlier on various factors which include thickness of the film, nature of substrates, composition, temperature etc. A crucial factor favouring the stabilization of the pyrochlore structure is a deficiency of Pb in the film (Tuttle *et al* 1990; Carim 1991; Krupanidhi *et al* 1992). This is because in the defect pyrochlore structure, represented by A₂B₂O_{7-x}, the BO₆ octahedra are linked together and provide stability to the structure while –A–O chains penetrate the BO₆ octahedra but do not contribute much to the rigidity of the structure (Subramanian *et al* 1983). The pyrochlore thus can tolerate a large deficiency of A (Pb) and oxygen.

A loss of Pb usually occurs during the sintering of Pb based ceramics due to a high volatility of PbO at the sintering temperature (1250°C) (Buckner and Wilcox 1972; Lucata *et al* 1985). In the case of thin films, Pb can additionally be lost

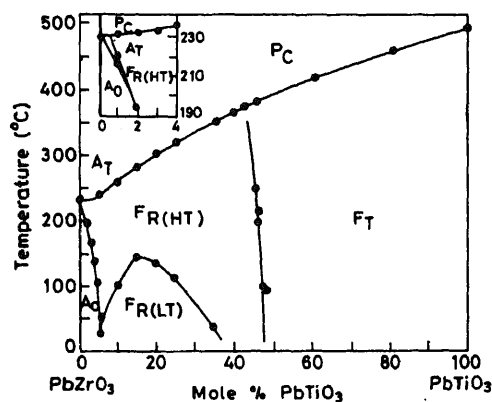


Figure 1. Phase diagram of lead zirconate-lead titanate solid solution.

Table 3. Summary of literature data on phases in PZT film.

Composition	Treatment	Thickness	Substrate	Phase	Ref.
Pb(Zr _{0.5} Ti _{0.5})O ₃	600°C/1/hr	0.1 µm	7059 glass	Pyro	Takahashi <i>et al</i> (1992)
		0.4 µm	7059 glass	Pero	
		0.1 µm	Pt, Al ₂ O ₃	Pero	
		0.4 µm	Pt, Al ₂ O ₃	Pero	
PZT	15 mins at (i) 450°C (ii) 550°C (iii) 600°C (iv) 650°C	0.17 µm	sapphire	Amorphous Pyro Pyro + pero Pero	Kwok <i>et al</i> (1992)
PLZT	(i) 600°C/30 min	0.5 µm	Au, Pt, Al ₂ O ₃	Pero	Seth and Schulze (1990)
	(ii) 800°C/30 min	0.1 µm	Fused SiO ₂	No crystal	
	(iii) 800°C/30 min	0.1 µm	Si (100) and Si (111)	No crystal	

due to its diffusion into the substrate (Lipiles *et al* 1986; Seth and Schulze 1990). Such diffusion is likely to be greater in amorphous substrates as compared to inert crystalline substrate. It has been proposed (Majumder *et al* 1994) that the deficiency of Pb caused by such diffusion may in fact be responsible for the retention of the pyrochlore phase rather than any 'epitaxial' effect proposed in some reports (Takahashi *et al* 1990; Krupanidhi *et al* 1992).

To test this idea we have used Rutherford back scattering (RBS) in conjunction with X-ray diffraction (XRD) to investigate interfacial phenomena controlling phase formation in thin films of PZT of morphotropic composition on two typical substrates-fused quartz and sapphire. In this paper we present experimental evidence regarding the role of diffusion at the interface.

2. Experimental

Thin films of approximately same thicknesses (70 to 390 nm) were deposited on amorphous quartz and (1120) sapphire by a sol-gel technique described elsewhere (Majumder *et al* 1994). The composition of the sol was taken to be near the MPB region but with 5 mole% excess PbO i.e. $\text{Pb}_{1.05}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$. The sol was prepared using lead acetate, zirconium-*n*-propoxide, titanium-4-butoxide, isopropanol, water and ethylene glycol (to avoid cracking of the film). The relative amounts of various chemicals used in a typical sol are given in table 4. The film was deposited by spin coating at 8000 rpm. The coated substrate was dried at 80°C for 20 min. It was then heated at 5°C/min to 400°C and held at that temperature for 30 min to drive off the organics. The temperature was then raised to 600°C and maintained for 6 h followed by furnace cooling. The thickness of the film was measured by a surface profilometer (Alpha Step-100, Tencor Instruments USA) and phases of the films were evaluated by X-ray diffractometer (Rich-Seifert Iso-Debyelex 2002, Germany) using Cu K α radiation with a monochromator. RBS spectra were obtained using 1.7 MeV He⁺ ions from 2 MeV Van-de-Graff accelerator facility. The back scattered particles were detected using a silicon surface barrier detector kept at a backscattering angle of 150°. All RBS spectra were analyzed using the versatile RUMP software package (Doolittle 1985, 1986).

3. Results and discussion

Figure 2 shows the X-ray diffractograms for films of different thicknesses (a) on sapphire and (b) on fused quartz substrates. All the films on sapphire are in perovskite phase irrespective of thickness. We have checked it down to 450 Å on sapphire substrate. On the other hand the first two relatively thinner films on quartz (IIA and IIB) do not show any peak whereas sample IIC which is 3900 Å thick yields a pyrochlore phase. We have also observed, in agreement with earlier reports, that films thicker than 1.5 µm on quartz yield a perovskite phase. Note that the failure to obtain XRD peaks in samples IIA and IIB cannot be due to decreased volume of the material as seen by X-ray since on sapphire the sample as thin as 450 Å yields peaks corresponding to the perovskite phase under similar conditions.

Figure 3a shows RBS spectra—both experimental (dotted) and simulated (solid line)—for the films on sapphire substrate. The structures used for simulation are given in table 5. Simulated compositions of the film agree with nominal composition

Table 4. Typical composition of the coating sol used in the present study.

Material	Moles
Lead acetate	1.05
Acetic acid	6.60
Zirconium- <i>n</i> -propoxide	0.53
Titanium-4-butoxide	0.47
Water	0.52
Ethylene glycol	0.44

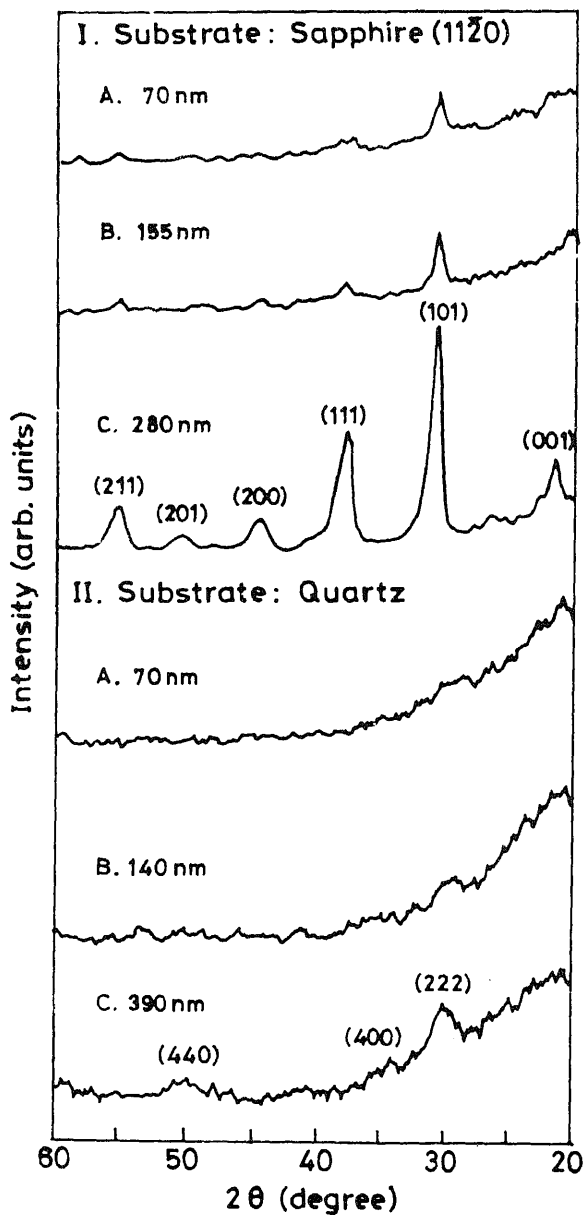


Figure 2. X-ray diffractograms of films on I : sapphire (1120) and II : quartz, the perovskite phase is obtained on sapphire and the pyrochlore phase on quartz.

except for a small difference in Pb concentration. The thicknesses of simulated layers are also in agreement with profilometer measurements.

Figure 3b shows RBS spectra of the films on quartz substrate. In contrast with sapphire substrate, where the RBS spectra could be perfectly simulated using only one layer, it was found necessary to invoke multilayer structures of differing

compositions to obtain simulated RBS spectra shown by solid lines in figure 3b (i-iii). These structures are listed in table 6.

For thinner films the high energy peaks corresponding to Pb, Zr and Ti are well separated and absolute concentrations of these heavy elements can easily be

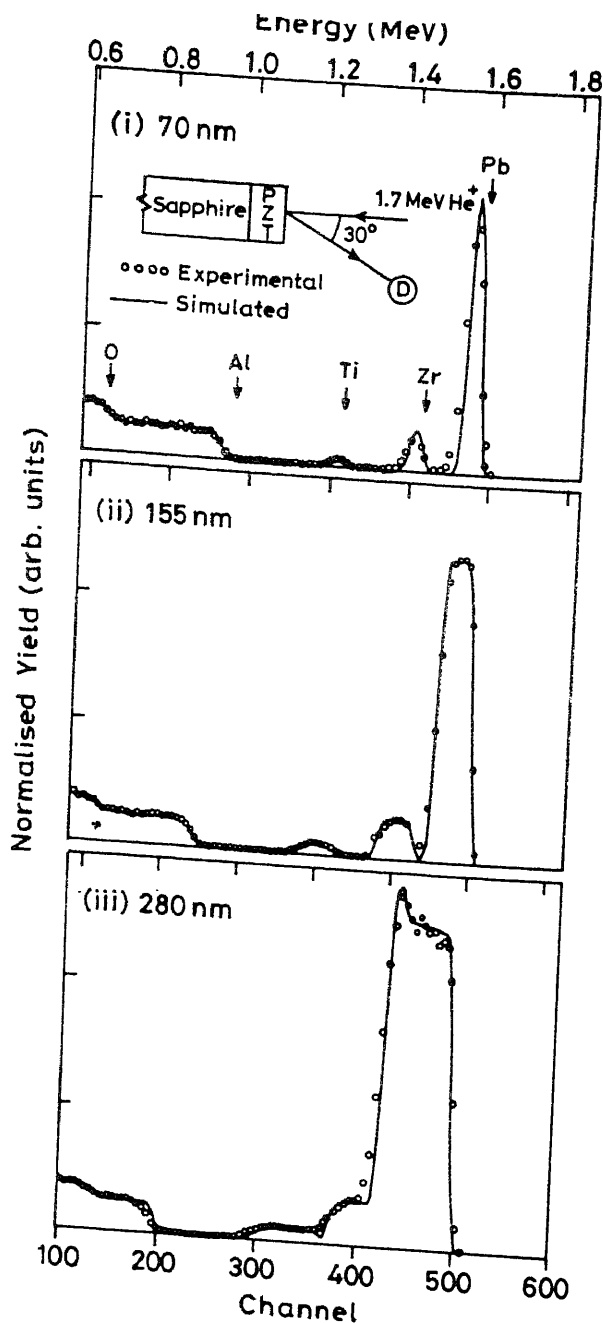


Figure 3a. For caption, see p. 1011.

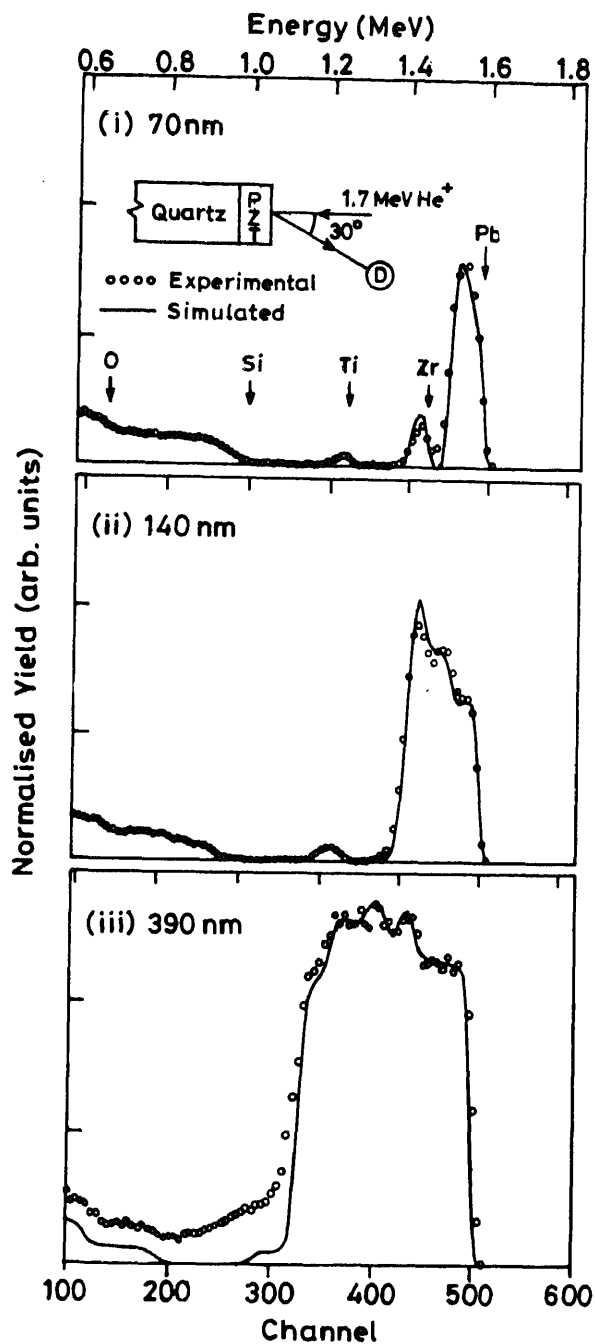


Figure 3. a–b. a. RBS spectra of PZT films of different thicknesses on sapphire (i) 70 nm, (ii) 155 nm, (iii) 280 nm; the arrows indicate the surface positions of the element shown and b. RBS spectra of PZT films of different thicknesses on fused quartz (i) 70 nm, (ii) 140 nm, (iii) 390 nm; the arrows indicate the surface positions of the element shown.

Table 5. Summary of X-ray and RBS results for PZT films on sapphire (1120).

Sample no.	Film thickness (nm)	X-ray phase	RBS simulation structure	Layer thickness (Å)	Layer #
IA	70	Perovskite	Pb _{0.92} Zr _{0.53} Ti _{0.47} O ₃	700	1
			Al ₂ O ₃	15000	2
IB	155	Perovskite	Pb _{0.92} Zr _{0.53} Ti _{0.47} O ₃	1550	1
			Al ₂ O ₃	20000	2
IC	280	Perovskite	Pb _{1.0} Zr _{0.53} Ti _{0.47} O ₃	3000	1
			Al ₂ O ₃	20000	2

Table 6. Summary of X-ray and RBS results for PZT films on fused quartz.

Sample no.	Film thickness (nm)	X-ray phase	RBS simulation structure	Layer thickness (Å)	Layer #
IIA	70	No pattern	Pb _{0.32} Zr _{0.53} Ti _{0.47} O ₃	400	1
			Pb _{0.40} Zr _{0.53} Ti _{0.47} O _{2.5} Si _{0.5}	400	2
			Pb _{0.36} Si _{1.0} O _{2.25}	800	3
			SiO ₂	20000	4
IIB	140	No pattern	Pb _{0.38} Zr _{0.53} Ti _{0.47} O ₃	950	1
			Pb _{0.38} Zr _{0.53} Ti _{0.47} O _{2.5} Si _{0.5}	400	2
			Pb _{0.36} Si _{1.0} O _{2.25}	2200	3
			SiO ₂	20000	4
IIC	390	Pyrochlore	Pb _{0.85} Zr _{0.53} Ti _{0.47} O ₃	3000	1
			Pb _{0.82} Zr _{0.53} Ti _{0.47} O ₃	200	2
			Pb _{0.71} Zr _{0.53} Ti _{0.47} O _{2.5} Si _{0.5}	400	3
			Pb _{1.4} Si ₂ O ₆	1000	4
			Pb _{1.2} Si ₂ O ₆	2000	5
			Pb _{1.0} Si ₂ O ₆	1200	6
			SiO ₂	10000	7

calculated. These are within 5% of those obtained from simulated spectra. No loss of Zr and Ti from the samples is observed. The discrepancy in total Pb concentration is less than 10% for films on quartz just as in the case of sapphire substrates. This Pb loss can be attributed to volatilization during heat treatment for both the

cases. For the individual layers in case of quartz substrates, simulation can provide only ratios of various elements and hence it is important to fix at least one ratio from some other argument. The initial simulations showed that Zr and Ti concentrations do not change after heat treatment. The insignificant amount of tailing towards the low energy ends of Zr and Ti peaks can be attributed to depth undulation at the interface. Therefore Zr/Ti ratio is fixed at the nominal composition (i.e. 0.53/0.47) and all other ratios are adjusted accordingly.

For the two relatively thinner samples on quartz, IIA and IIB, three layers had to be invoked in which top layer (layer 1) is only lead deficient while layer 2, in addition, shows presence of Si. The top two layers containing nominal Zr/Ti ratio add up approximately to the thickness of the film obtained by profilometer measurements. This shows that the inter diffusion of Pb and Si has occurred across the original interface between PZT layer and quartz substrate leading most probably to the formation of a lead silicate compound (e.g. PbSiO_3 or PbSi_2O_7). Layer 3 can then be viewed as arising out of lead silicate dispersed in quartz matrix. The presence of layer 2 in the structures of IIA and IIB is an indication that there is formation of lead silicate in PZT layer as well, spanning several hundreds of angstroms. In other words, lead silicate is dispersed on both sides of the original interface between PZT layer and the quartz substrate producing a structure consisting of three apparent layers corresponding to Pb deficient PZT (layer 1) mixture of PZT and lead silicate (layer 2) and lead silicate dispersed in quartz matrix (layer 3). The comparative thicknesses of layers 2 and 3 show that lead diffusion occurs deep into the substrate whereas the diffusion of Si into PZT layer is small.

The simulated structure for thicker sample IIC on fused quartz is similar except for the fact that the top PZT layer is subdivided into two layers (layers 1 and 2) and the intermediate layer into three layers (layer Nos 4, 5, 6) reflecting Pb gradient in the whole structure as would be expected for a diffusing species. Layer No. 3 as earlier, is to be viewed as a part of PZT layer containing lead silicate phase. In this case the top three layers correspond approximately to the as-deposited film. Recall that no XRD peak was observed for cases of thinner films on quartz substrate (samples IIA and IIB) suggesting that these films are amorphous. RBS results on these films show that the Pb deficiency in the top PZT layer is as high as 60%. This suggests that these films are amorphous because Pb deficiency is too high for crystallization to occur. However in the thicker pyrochlore film (IIC) the overall Pb deficiency is 15% in the top PZT layer. It is reasonable to conclude that this level of Pb deficiency allows only a pyrochlore phase to form. When the film thickness is larger than $1.5\text{ }\mu\text{m}$ the composition of the layer is nearly same as the nominal composition and gives rise to a perovskite phase—this has been checked by RBS results on such thick films. In contrast, in the case of sapphire substrates, Pb is neither consumed in any interfacial reaction nor it diffuses into the substrate. The marginal Pb loss in this case can be explained by losses due to evaporation from the surface. Therefore the perovskite phase forms in PZT layers on sapphire irrespective of thickness down to $450\text{ }\text{\AA}$. The existence of unusually long tail of Pb peak towards the low energy side is most probably due to some cracks that appear in the thicker films. This feature is absent in case of crack-free thinner films.

RBS results thus show that Pb diffuses readily from PZT film to a depth of several thousand angstroms into the quartz substrate during the annealing step. This

results in a film highly depleted in Pb. This deficiency in Pb, rather than any substrate (epitaxial) effect is believed by us to be responsible for the retention of the amorphous or pyrochlore phase in the films on quartz. On sapphire where no such diffusion is found to occur, the perovskite phase forms readily.

The other observed effect relating to the phase formation can similarly be explained in terms of Pb deficiency in the film. Thus in thicker film, even on quartz, a perovskite phase is obtained because the top layer, which is the layer sampled in X-ray diffraction, does not develop Pb deficiency because of its large diffusion distance from the substrate. High Ti content (low Zr/Ti ratio) also favours the perovskite formation because Ti binds Pb more effectively as revealed by much lower activity of PbO in PbTiO_3 than in PbZrO_3 (Klee *et al* 1992), the loss of Pb thereby is less in composition with lower Zr/Ti ratio.

4. Summary

The difficulty in the formation of the perovskite phase in PZT films under certain experimental conditions is directly related to the extent of Pb loss from the film. If the Pb loss is not significant, then the perovskite structure forms easily. This is the case, for example, for thin films on substrates such as sapphire, platinum etc where the only Pb loss mechanisms is the volatilization of PbO during annealing. When Pb is also lost due to diffusion into the substrate or due to reaction with the substrate then the film may become heavily deficient in Pb and will not transform to the perovskite structure. Such diffusion is found to be substantial for amorphous substrates such as quartz.

For using the ferroelectric PZT film in non-volatile memory application, it is desirable to integrate the film with Si semiconductor technology. In view of the high reactivity of Pb with Si, and consequent difficulty in the formation of perovskite phase, it would be necessary to develop suitable diffusion barrier layers between PZT film and Si substrate. Development of such barrier layer is one of the most important issues in utilizing PZT film in memory application.

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Synthesis and study of structural, thermal, optical and magnetic properties of stabilized $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system ($0.01 < x < 0.30$)

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Abstract. A novel chemical passivation route is established to obtain microcrystalline solid solutions of binary oxide system $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ ($0.01 < x < 0.30$). During the passivation process, controlled thermal decomposition of manganous oxalate is carried out to obtain pure MnO and its subsequent reaction with NiO in oxygen-free nitrogen resulted in microcrystalline powder of these solid solutions. The powder is thoroughly characterized by various physicochemical techniques such as XRD, DTA/TG/DTG, diffused reflectance spectra, magnetic susceptibility, TEM, XPS etc. The observed processing–structure–property correlations confirmed the improved thermal stability of these powders (relative to pure MnO) in air. The important role of dopant paramagnetic Ni^{2+} ions in enhancing the passivation of the bulk Mn^{2+} species is explained on the basis of the formation of mixed oxide complex species on the surface of these microcrystalline powders.

Keywords. Stabilized MnO; chemical synthesis; surface passivation.

1. Introduction

It is well known that freshly prepared pure manganous oxide (MnO) is olive green in colour and highly unstable. Even at ambient conditions, it immediately oxidizes to its higher oxides like $\text{Mn}_2\text{O}_3/\text{MnO}_2$ (black in colour) on its exposure to air (Sidgewick 1950). This poses a difficult problem in carrying out a solid state reaction involving MnO to prepare high performance nickel manganese spinel ferrite. To overcome these difficulties it is essential to protect stoichiometric manganous oxide from its auto-oxidation. We have developed a novel processing route to prepare *in situ* solid solutions of MnO–NiO. In the present paper we report (i) synthesis of different stoichiometric compositions of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ ($0.01 < x < 0.30$) and (ii) its physicochemical characterization. The structural, thermal, optical, magnetic and surface-electronic properties have been investigated using various techniques such as XRD, DTA/TG/DTG, diffused reflectance spectra, magnetic susceptibility, TEM, XPS, etc and the experimental results and their analysis are presented.

2. Experimental

Figure 1 shows the flow diagram of the chemical passivation process developed in our laboratory. Four different compositions of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ solid solutions are essentially obtained by the controlled pyrolysis of manganous oxalate at 573 K and

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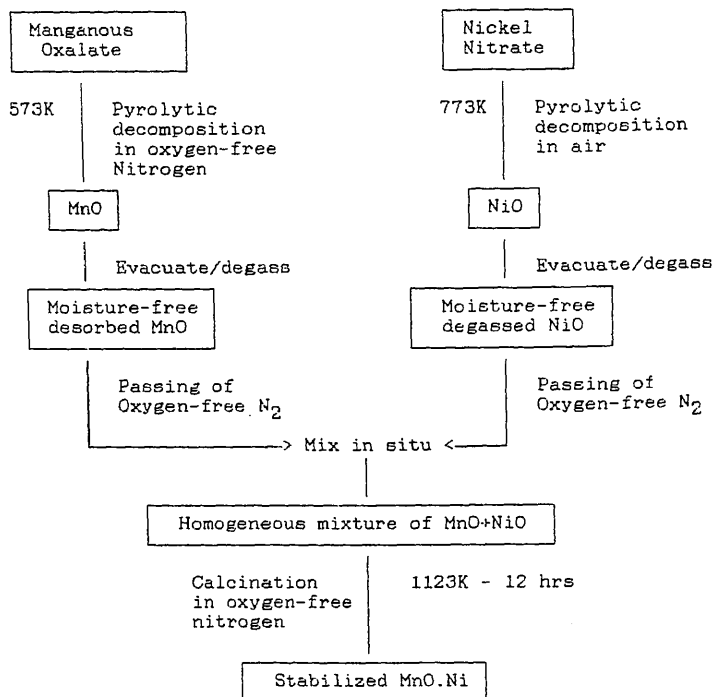


Figure 1. Preparation of 'stabilized MnO.Ni' system.

its subsequent reaction with NiO in oxygen-free nitrogen at 1123 K. The experimental details for $x = 0.01$ are given in detail below and the other remaining compositions are prepared in identical fashion.

For the preparation of $Mn_{1-x}Ni_xO$ with $x = 0.01$, thermal decomposition of the required quantity of manganese oxalate is carried out at 573 K in a slow continuous current of oxygen-free pure nitrogen using the silica unit (Murthy *et al* 1978). It is evacuated till it attains static vacuum and tested for 2–3 h. It is then cooled to room temperature and pure oxygen-free nitrogen is passed into the unit to release vacuum. The required quantity of nickel oxide, prepared earlier by thermal decomposition of nickel nitrate $[Ni(NO_3)_2]$ at 773 K in air and degassed separately is added to the freshly prepared MnO in the closed system and mixed homogeneously by careful shaking. It is calcined at 1123 K for 12 h in oxygen-free pure nitrogen. The unit is cooled to room temperature. The polycrystalline material thus obtained, is green in colour (hereafter referred to as 'stabilized MnO.Ni') and quite stable in air which can be easily handled without any fear of its oxidation on its exposure to air. There is no indication of oxygen chemisorption changing its colour from olive green to black. Weighed quantities of 'stabilized MnO.Ni' and NiO in the required proportions are mixed homogeneously and processed further to prepare various compositions with increasing x of $Mn_{1-x}Ni_xO$ system.

2.1 Physicochemical characterization

The polycrystalline solid solutions of $Mn_{1-x}Ni_xO$ ($0.01 \leq x \leq 0.30$) are characterized

using a variety of analytical techniques. Standard gravimetric methods of chemical analysis (Vogel 1964) are followed to determine the concentration of manganese and nickel in $Mn_{1-x}Ni_xO$ system. Powder X-ray diffractograms for all solid solutions are recorded using Phillips 1730 X-ray diffractometer. The cubic-lattice parameter a is determined from the observed d values and the corresponding intensities. DTA/TG/DTG studies are carried out using Netzsch (STA 409) thermal analyser in the temperature range 295 K to 1273 K in air. Diffused reflectance spectra have been recorded at room temperature on Pye-Unicam SP8-300 UV-VIS spectrometer. Magnetic susceptibility measurements are carried out using Cahn-1000 electrobalance with liquid nitrogen cryostat assembly in the temperature range 80 K to 300 K, calibrated with $HgCo(SCN)_4$. To determine the homogeneity of the composition and to study morphology, samples are examined with JEOL 1200 EX electron microscope with highest acceleration voltage of 120 kV and largest magnification of $\times 10^7$ in the bright field mode. For this study, following sample preparation technique is followed (Carr 1985). A small portion of the powdered sample is dispersed in isopropyl alcohol using ultrasonic bath. A microscope-grid is dipped in the suspension and after drying it becomes ready for viewing. X-ray photoelectron spectra are recorded on the calibrated VG Scientific ESCA-3 MK-II spectrometer with $AlK\alpha$ radiation.

3. Results and discussions

Following well-established analytical method (Vogel 1964), accurate wet-gravimetric analyses have been carried out to establish purity and homogeneity of solid solutions. After establishing their identities, these polycrystalline materials have been characterized for their properties using different techniques.

3.1 XRD

Powder X-ray diffractograms of all solid solutions of $Mn_{1-x}Ni_xO$ ($0.01 \leq x \leq 0.30$) show a characteristic pattern of single phase rock-salt type crystal structure (Rao and Subba Rao 1974). Cubic lattice parameters of these solid solutions are computed from the careful intensity analysis of X-ray diffractograms and are presented in table 1. The lattice parameter decreases linearly with increasing x obeying Vegard's law (Kaelble 1967) and is attributed to the substitutional occupancy of Mn^{2+} ions (ionic radius = 0.080 nm) by Ni^{2+} ions (ionic radius = 0.069 nm) in the lattice. Our experimental results agree with the earlier reported results that MnO and NiO form solid solutions in different proportions (Hahn and Muan 1961; Barret and Evans 1964; Cheetham and Hope 1983).

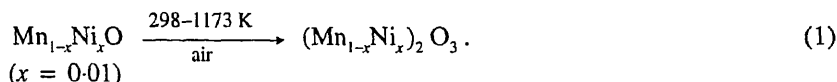
3.2 TG/DTG/DTA studies

To study the thermal behaviour of the solid solutions and its dependence on concentration of nickel, x , in the system $Mn_{1-x}Ni_xO$ ($0.01 < x < 0.30$), TG/DTG/DTA curves are simultaneously recorded with the heating rate of 10 K/min in the temperature range 298–1273 K in air. Figure 2 shows a typical thermogram for the

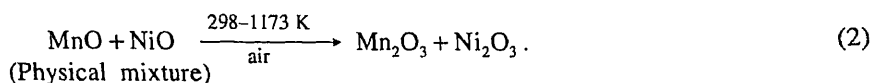
Table 1. Cubic lattice parameter a and thermal stability of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system: DTA-TGA-DTG studies.

Concentration of nickel (x) in $\text{Mn}_{1-x}\text{Ni}_x\text{O}$	Cubic lattice parameter a (nm)	Maximum oxygen uptake (%) $\text{MnO} \rightarrow \text{Mn}_2\text{O}_3$ and $\text{NiO} \rightarrow \text{Ni}_2\text{O}_3$		% of Mn^{2+} species	
		Theoretical	Experimental from TG	Oxidized	Unoxidized
0.01	0.4440	11.27	10.26	91.04	8.96
0.10	0.4419	11.22	10.22	91.09	8.91
0.20	0.4399	11.16	9.88	88.53	11.47
0.30	0.4377	11.10	9.67	87.12	12.88

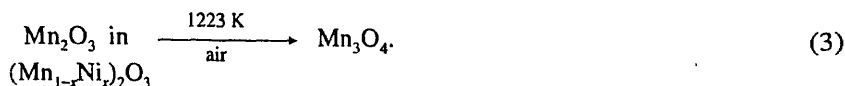
solid solution with lowest conc. $x = 0.01$. It is observed that the sample is gaining weight continuously as indicated by the slow and steady rise in the TG/DTG curves in the temperature range 298–1173 K. The DTA curve also shows a very broad exothermic peak up to 1173 K. This is in contrast with the very fast oxidation of pure MnO i.e. spontaneous reaction taking place in air (Sidgewick 1950) even at room temperature. This gain is understood in terms of the very slow and controlled rate of oxidation as envisaged by the following equation:



The observed gain from the TG/DTG curve is 10.26% which can be compared with complete thermal oxidation of the proportionate physical mixture of MnO plus NiO in air occurring as follows:



This mixture (with same proportion of MnO:NiO as in (1)) has 11.27% uptake of oxygen on its complete oxidation. The observed difference in the % of uptake of oxygen (% of uptake of oxygen in (1) < (2)) shows that 91.04% of Mn^{2+} species present in the solid solution are converted to its higher oxide. It is quite clear now that the remaining 8.96% Mn^{2+} species are not converted to its higher oxide. The % of unconverted species have been attributed to the controlled oxidation of the $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system as a whole. On further heating up to 1223 K a loss in weight of the sample is observed from the TG and the sharp peak of DTG curve. It is an endothermic reaction as also indicated by a sharp DTA peak. The observed % loss in weight is attributed to the reduction of Mn_2O_3 present in the $(\text{Mn}_{1-x}\text{Ni}_x)_2\text{O}_3$ to Mn_3O_4 represented as in (3) (Sidgewick 1950):



No further change in weight of the sample or occurrence of any reaction is observed

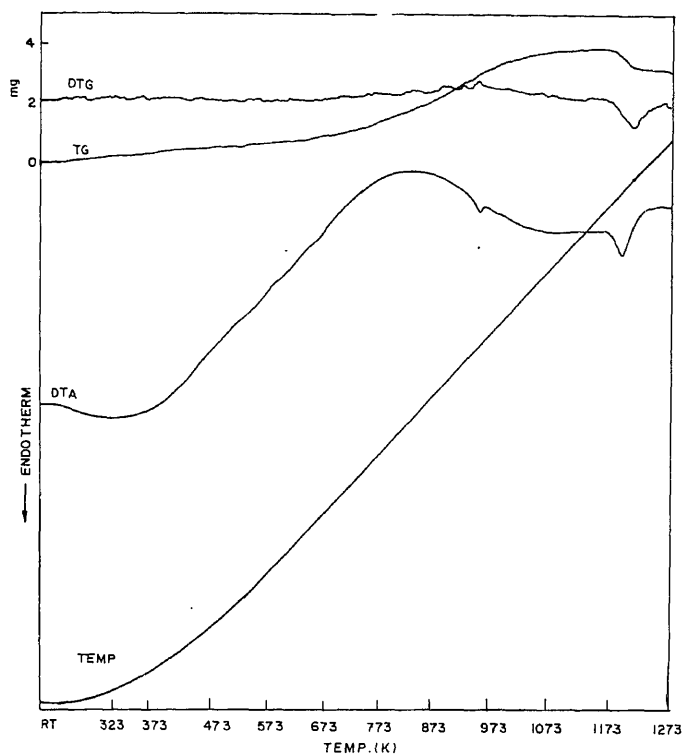


Figure 2. Thermogram of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ ($x = 0.01$) system.

on further heating the sample in air up to 1273 K. Similar plots have been observed for the remaining compositions of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system and the results are presented in table 1. It shows that the thermal stability (slow rate of oxidation and the % of Mn^{2+} species remaining unoxidized) increases with increasing x . The results will be further substantiated using optical properties, magnetic susceptibility, TEM and XPS studies and will be discussed in the later sections.

3.3 Diffused reflectance spectra

The diffused reflectance spectra of the solid solutions, with $x = 0.01$, 0.2 and 0.3 in $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system are recorded at room temperature in the range 380–760 nm (figure 3). All the spectra exhibit characteristic absorption peaks which can be easily assigned on the basis of Tanabe–Sugano diagrams (Tanabe and Sugano 1954) for d^5 and d^8 ions (figure 4). For example, there are three distinct absorption peaks at 16393 cm^{-1} (610 nm), 20833 cm^{-1} (480 nm), 23809 cm^{-1} (420 nm), observed for the sample with $x = 0.01$ in $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system (figure 3a). The absorption peak at 20833 cm^{-1} (480 nm) is clearly observed for the sample with lowest concentration, $x = 0.01$ only. Its clear resolution is not observed for the remaining samples with higher concentrations. These observed peaks for the sample with $x = 0.01$ are assigned to

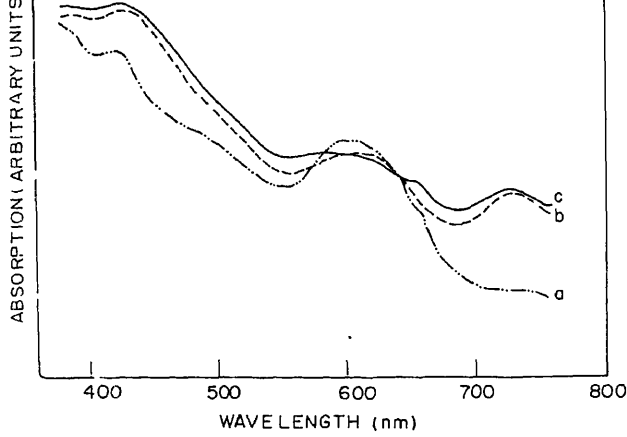


Figure 3. Reflectance spectra of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system (a. $x = 0.01$, b. $x = 0.2$ and c. $x = 0.3$).

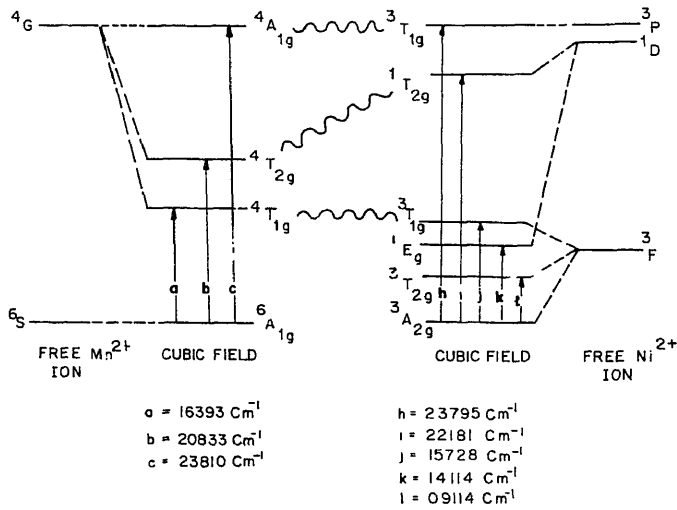


Figure 4. Energy level diagram for d^5 (Mn^{2+}) and d^8 (Ni^{2+}) ions in octahedral field.

$${}^6A_1 \rightarrow {}^4T_1, {}^6A_1 \rightarrow {}^4T_2, {}^6A_1 \rightarrow {}^4E,$$

transitions of the ${}^6S_{5/2}$ ground state of Mn^{2+} ions in nearly undistorted octahedral field. These transitions agree very well with the earlier reported optical studies (Pratt and Coelho 1959; Deshpande *et al* 1985; Bakare *et al* 1991) on similar systems. Additional resolvable peaks can be assigned to the Ni^{2+} ions (figures 3a–c). These transitions are ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (23795 cm^{-1}), ${}^3A_{2g} \rightarrow {}^1T_{2g}$ (D) (22180

cm^{-1}), ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (15730 cm^{-1}), ${}^3A_{2g} \rightarrow {}^1E_{1g}$ (D) (14115 cm^{-1}) and ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (F) (9115 cm^{-1}). Experimental data are presented in table 2 for the three samples with different values of x in the $Mn_{1-x}Ni_xO$ system. It is noticed that there is hardly any shift in the transitions of Mn^{2+} ions. This indicates that the local order and electronic structure of Mn^{2+} ions in the surrounding oxygen octahedra remain nearly intact. In other words, the distance between manganese and oxygen, r_{Mn-O} is constant maintaining the ligand parameter, Dq , unchanged. Since Dq is proportional to r^{-5} and r_{Mn-O} is half of its lattice parameter, it is to be expected that the lattice parameter, a , will remain constant with increasing x . However, a small variation in a from 0.4440 nm to 0.4377 nm for $x = 0.01$ to 0.3 is observed which can be attributed to the smaller ionic radii of Ni^{2+} ions (0.069 nm) than Mn^{2+} (0.080 nm) ions. Moreover, it is such a small order that there is hardly any change in Dq so as to cause a shift of the Mn^{2+} peaks in the absorption spectra. In contrast,

$${}^6A_{1g} \rightarrow {}^4T_{2g} \text{ and } {}^6A_{1g} \rightarrow {}^4A_{1g},$$

peaks exhibit considerable shift with increasing x . This results from the direct intermixing and coupling of the $Mn-{}^4T_{2g}$ (G) and $Ni-{}^1T_{2g}$ (D) and $Mn-{}^4A_{1g}$ (G) and $Ni-{}^3T_{1g}$ states (Lever 1984) respectively. Similarly, a small shift is also observed in the peak position of the ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (Mn^{2+} transition) due to intermixing and coupling of $Mn-{}^4T_{1g}$ (G) and $Ni-{}^3T_{1g}$ (F) states. These results from the diffused reflectance spectra thus clearly show that (i) Mn^{2+} ions are occupying the nearly perfect local lattice environment of oxygen octahedra, and (ii) the formation of well defined $Mn_{1-x}Ni_xO$ solid solutions.

3.4 Magnetic susceptibility measurements

Magnetic susceptibility measurements of $Mn_{1-x}Ni_xO$ solid solutions with $x = 0.01$, 0.1 , 0.2 and 0.3 have been carried out in the temperature range 77 to 300 K . Representative plots of $1/\chi_g$ vs T for the $Mn_{1-x}Ni_xO$ system with $x = 0.01$ and 0.3 are given in figure 5. All the samples showed a minimum value of $1/\chi_g$ at a temperature which is associated with the antiferromagnetic ordering temperature,

Table 2. Absorption spectra of $Mn_{1-x}Ni_xO$.

Transitions from ground state	Conc. of nickel (x) in $Mn_{1-x}Ni_xO$				Transitions from ground state
${}^6A_{1g}$ of MnO	0.00	0.01	0.20	0.30	${}^3A_{2g}$ of NiO
		13660	13735	13775	9115 $\rightarrow {}^3T_{2g}$ (F)
		15245	15175	15175	14115 $\rightarrow {}^1E_g$ (D)
${}^4T_{1g}$ (G) $\leftarrow 16393$		16555	16510	16500	15730 $\rightarrow {}^3T_{1g}$ (F)
${}^4T_{2g}$ (G) $\leftarrow 20833$		20160	20325	20325	22180 $\rightarrow {}^1T_{2g}$ (D)
${}^4A_{1g} E_g$ (G) $\leftarrow 23810$		23810	23255	23255	23795 $\rightarrow {}^3T_{1g}$ (P)

(Frequency in cm^{-1}).

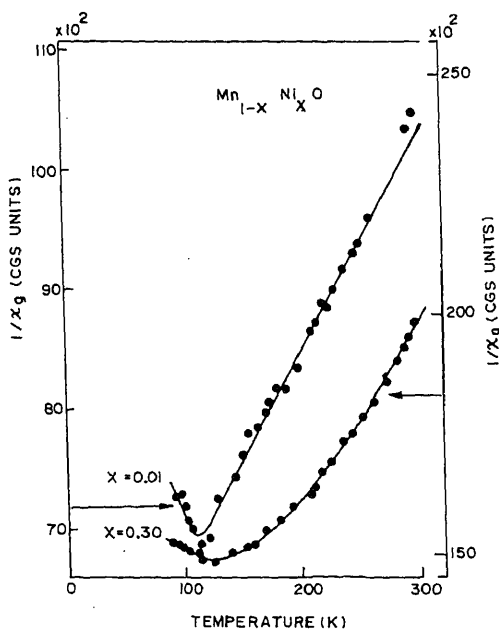


Figure 5. $1/\chi_g$ vs T plots of $Mn_{1-x}Ni_xO$.

T_N . The Weiss temperature, θ , is obtained by extrapolating the paramagnetic linear region of the $1/\chi_g$ vs T plot to give an intercept on the temperature axis. The values of T_N , θ , θ/T_N and μ_{eff} computed from the slopes of the plots of $1/\chi_g$ vs T above 200 K are presented in table 3. It is observed from the plots that the minimum for $x = 0.01$ in $Mn_{1-x}Ni_xO$ system is sharp and broadens with increasing x and T_N is also same as/very close to that of cubic MnO indicating that host lattice is in tact and T_N shifts to higher temperature with increasing x , obeying Curie-Weiss law. The broad minimum observed in the inverse susceptibility curve, similar to that observed in $Mn_{1-x}Zn_xO$ and $Mn_{1-x}Mg_xO$ systems (Deshpande *et al* 1982), can be explained as due to exchange interactions occurring in the rock-salt crystal structure. In the case of pure MnO , the 90° Mn-O-Mn(NN) and direct Mn-Mn interactions are possible in an antiferromagnetic ordering since d orbitals of Mn^{2+} are half-filled. On the other hand, such direct Ni-Ni exchange is not possible in NiO as the t_{2g} orbitals are full and only 90° cation-anion-cation (NN) interaction is possible (Goodenough 1963). Moreover, an antiferromagnetic (NNN) interaction involving only e_g orbitals is possible in both MnO and NiO . The present system of $Mn_{1-x}Ni_xO$ involves both t_{2g} and e_g orbitals of Mn^{2+} ($t_{2g}^3 e_g^2$) and Ni^{2+} ($t_{2g}^6 e_g^2$) exhibiting complex magnetic interaction which may have to be thoroughly studied in the low temperature-high field experiments. It results in (i) a broad minima seen in the plots of $1/\chi_g$ vs T in $Mn_{1-x}Ni_xO$ system and (ii) an increasing trend in θ/T_N with increasing x . This behaviour is similar to the trend reported earlier by Aviazov and Gurov (1974) involving the increase in ferromagnetic coupling (Cheetham and Hope 1983) between Mn^{2+} and Ni^{2+} ions indicating the absence of noncollinear oblique antiferromagnetic (OAF) phase (Katsumata *et al* 1979) occurring in the system.

Table 3. Effect of conc. of Ni(x) on the magnetic properties of $Mn_{1-x}Ni_xO$ system.

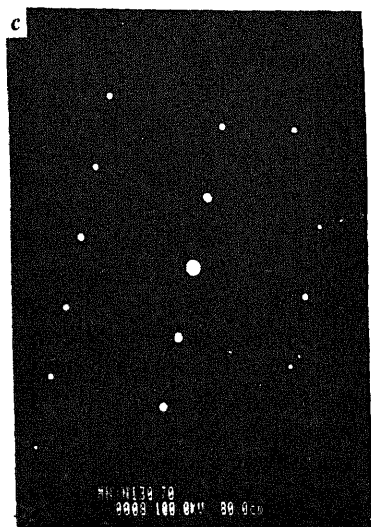
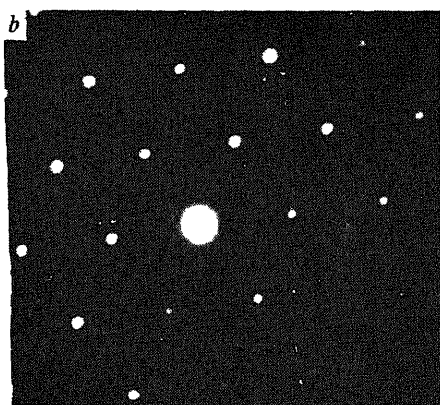
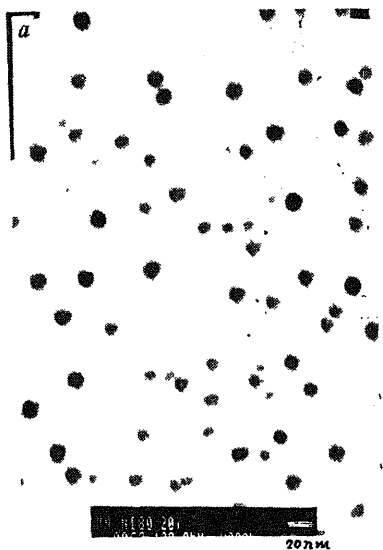
Conc. of Ni(x) in $Mn_{1-x}Ni_xO$	μ_{eff} (BM) at 300 K	θ (K)	T_N (K)	θ/T_N
0.01	4.76	110	120	0.917
0.10	3.68	112	120	0.933
0.20	3.63	154	123	1.252
0.30	3.76	164	127	1.291

3.5 Electron microscopy and EDS analysis

The morphology of the sample with $x = 0.3$ in $Mn_{1-x}Ni_xO$ system is shown in figure 6a. The shape of the particles is almost spherical and they are well-separated. It indicates that there is no ferromagnetic interaction between these particles. The particles size distribution is obtained from an electron micrograph at 200 K magnification. The average particle size, observed for all the samples, is ≈ 15 – 18 nm. The selected area electron diffraction pattern (SAD) of the sample with $x = 0.3$ in $Mn_{1-x}Ni_xO$ system is shown in figure 6b with zone axis $[100]$, figure 6c with zone axis $[310]$ and figure 6d key to figure 6c. It is comparable with cubic unit cell (FCC) having cubic lattice parameter, $a = 0.438$ nm. This matches well with the cubic lattice parameter a computed from the powder X-ray diffraction pattern. A typical EDS (KeveX) analysis of the representative sample with $x = 0.3$ is presented in figure 7. The ratio of intensity of Ni:Mn counts indicates the desired stoichiometric ratio. However, in addition to these two elements, small quantities of copper and chromium are also detected by EDS. The impurities are from the specimen holder rather than the sample.

3.6 X-ray photoelectron spectroscopy

To differentiate between the bulk and surface oxidation of the solid solution during its exposure to air at room temperature a highly surface sensitive technique such as X-ray photoelectron spectroscopy (XPS) was used. X-ray photoelectron spectra of representative samples were recorded using an $AlK\alpha$ radiation source (1486.6 eV). Initially, full general scans (1000 eV) were recorded to check all appropriate peaks corresponding to the expected chemical composition on the surface. High resolution XPS scans were recorded over a narrower energy scale (30 eV) for the samples with $x = 0.10$ before (figures 8a and 9a) and after heating above 330 K for 2 h (figures 8b and 9b) for nickel (2p), manganese (2p) and oxygen (1s) levels. Table 4 presents XPS data (before and after heating the samples in air) of characteristic peaks usually employed in assigning the oxidation states in transition metal oxides. From characteristic BE values ($2p_{3/2}$) and ΔE_{3s} of Mn^{3+} in Mn_2O_3 (Fadley and Shirley 1970; Carver *et al* 1972; Oku *et al* 1975; Wertheim *et al* 1975; Rao *et al* 1979; De Boer *et al* 1982; Foord *et al* 1984; Zhao and Young 1984) and Ni^{2+} in NiO (Kim and Ninoguard 1974), the observed peaks are assigned to Mn^{3+} and Ni^{2+} species present on the surface (30–40 Å) with high concentrations.



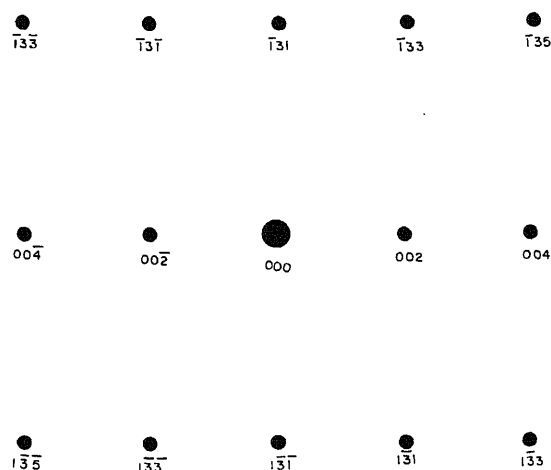


Figure 6. TEM of $Mn_{1-x}Ni_xO$ ($x = 0.3$) system. a. Bright field micrograph, b. SAD with zone axis $[100]$, c. SAD with zone axis $[310]$ and d. key to (6c).

The presence of Mn^{3+} and Ni^{2+} species on the surface indicates a possible formation of a mixed $NiO-Mn_2O_3$ phase. On heating the samples in air around 330 K, characteristic shifts in Mn ($3s$), Mn ($2p_{3/2}$) and Ni ($2p_{3/2}$) levels are clearly observed. By comparing with reported data (Fadley and Shirley 1970; Carver *et al* 1972; Oku *et al* 1975; Wertheim *et al* 1975; Rao *et al* 1979; De Boer *et al* 1982; Foord *et al* 1984; Zhao and Young 1984; Deshpande *et al* 1985), of shifts in Mn-O system and Ni-O system (Kim and Ninoguard 1974), these peaks are assigned to Mn^{4+} species and Ni^{3+} species (table 4) present on the surface. It is clear from these observations that the Mn_2O_3-NiO type mixed phase, present on the surface is oxidized to MnO_2 and Ni_2O_3 (table 4). A structural vacancy associated model (Deshpande *et al* 1985; Bakare *et al* 1991) has been earlier proposed by our laboratory to explain the chemical passivation process for $Mn_{1-x}M_xO$ systems ($M = Zn, Mg$). However, this phenomenon of oxidation in the case of $Mn_{1-x}Ni_xO$ is different from that occurring in the case of samples from the $Mn_{1-x}Zn_xO$ and $Mn_{1-x}Mg_xO$ systems (Deshpande *et al* 1985; Bakare *et al* 1991). In the case of $Mn_{1-x}Zn_xO$ system (Deshpande *et al* 1985), the Mn_2O_3-ZnO mixed phase is oxidized on heating at $T >$ stabilization temperature and shows the presence of MnO_2 on the surface, whereas Zn^{2+} ions diffuse into the bulk MnO . Similarly in the case of $Mn_{1-x}Mg_xO$ system (Bakare *et al* 1991), Mg^{2+} ions present on the surface as $MgO-Mn_2O_3$ mixed phase diffuse into the bulk MnO . The present system of $Mn_{1-x}Ni_xO$ is different from the above referred two systems, obviously due to the fact that Ni^{2+} gets oxidized to Ni^{3+} , instead of diffusing inside the bulk MnO like Zn^{2+} , Mg^{2+} ions. This results into slow oxidation of the whole sample. In short, highly active sites (surface) are preferentially occupied by Ni^{2+} ions, which together with Mn^{3+} ions form a mixed phase $NiO-Mn_2O_3$ on the surface. This surface phase prevents the subsequent oxidation of bulk MnO .

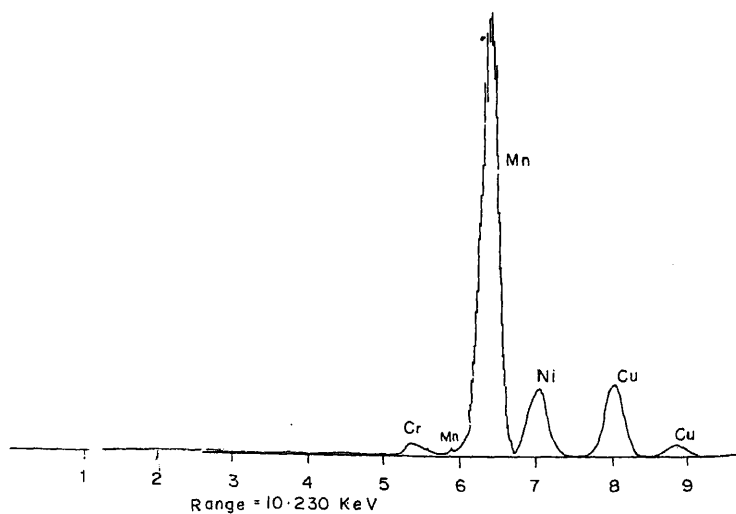


Figure 7. EDS analysis of the $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ ($x = 0.3$) system.

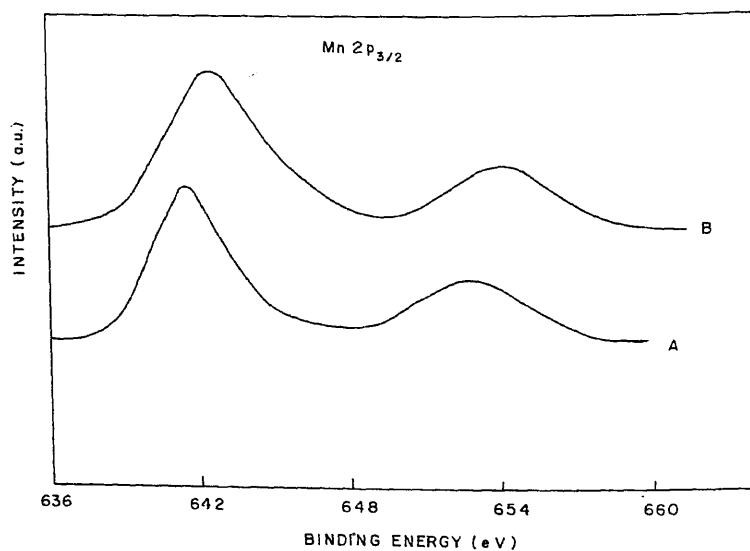


Figure 8. XPS of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ ($x = 0.10$) before (A) and after heating at 330 K in air (B) for Mn-levels.

4. Conclusion

In summary, we have shown that *in situ* solid solutions $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ ($0.01 < x < 0.30$) system can be successfully prepared. X-ray diffraction studies reveal the formation of single cubic phase and linear decrease of the lattice parameter with increasing

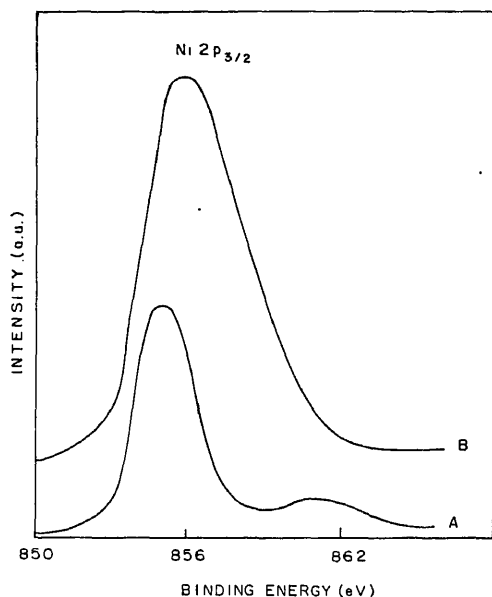


Figure 9. XPS of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ ($x = 0.10$) before (A) and after heating at 330 K in air (B) for Ni-levels.

Table 4. XPS data on $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ before and after heating () at 330 K for 2 h in air.

Sample with conc (x) in $\text{Mn}_{1-x}\text{Ni}_x\text{O}$	Binding energy (BE) eV ± 0.2 eV						
	Mn					Ni	O^{2-}
	3s	ΔE 3s	$2p_{3/2}$	$2p_{1/2}$	ΔE 2p	$2p_{3/2}$	1s
0 (MnO)	84.6	6.2	640.9	652.7	11.8	—	529.9
1 (NiO)	—	—	—	—	—	854.6	529.6
0.01	83.9 {84.6}	5.6 {4.8}	641.6 {642.6}	653.4 {653.2}	11.8 {11.6}	854.8 {855.6}	529.6 {529.6}
0.10	83.4 {84.3}	5.4 {4.8}	641.6 {642.6}	653.4 {653.2}	11.8 {11.6}	854.8 {855.6}	529.6 {529.6}
0.20	83.4 {84.3}	5.4 {4.8}	641.6 {642.6}	653.4 {653.2}	11.8 {11.6}	854.8 {855.6}	529.6 {529.6}
0.30	83.6 {84.0}	5.2 {4.6}	641.6 {642.6}	653.4 {653.4}	11.8 {11.6}	854.8 {855.6}	529.6 {529.6}

x (nickel concentration). DTA-TG-DTG studies show their relative thermal stability in air and process of very fast oxidation of pure MnO is considerably controlled to a great extent. The diffused reflectance spectra indicates the presence of a doublet band due to an extensive mixing of Ni^1E_g (D) and Ni^3_{2g} (F) transitions

and exhibit characteristic absorption peaks of both MnO and NiO with a shift in their positions due to intermixing of some of the transitions of Mn^{2+} and Ni^{2+} ions in cubic field. Analysis of the magnetic susceptibility data of $Mn_{1-x}Ni_xO$ system indicated involvement of both t_{2g} and e_g orbitals of Mn^{2+} ($t_{2g}^3 e_g^2$) and Ni^{2+} ($t_{2g}^6 e_g^2$) exhibiting complex magnetic interaction. It also suggests absence of a non-linear oblique antiferromagnetic phase in the system. T_N indicates that host lattice of cubic MnO remains intact. TEM study shows that the samples have well-separated spherical particles (size ≈ 15 – 18 nm). It has been qualitatively established by using EDS analysis that weighed in/initial stoichiometry of the compositions is well preserved. Cubic lattice parameters computed using electron diffraction patterns agree well with those observed by XRD. The presence of Mn_2O_3 –NiO (mixed phase) on the surface of $Mn_{1-x}Ni_xO$ system prevents the subsequent oxidation of bulk MnO. XPS studies show the formation of mixed Mn_2O_3 –NiO phase present on the surface. This phase acts like a passivation layer preventing the fast oxidation (rate of uptake of oxygen) of the solid solutions.

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EXAFS and MAS NMR studies of sodium molybdophosphate and sodium tungstophosphate glasses

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Abstract. The local order around molybdenum and tungsten atoms in various sodium molybdophosphate and sodium tungstophosphate glasses has been investigated using extended X-ray absorption fine structure (EXAFS). Both molybdenum and tungsten atoms are present in six-coordinated environment in these glasses. Magic angle spinning nuclear magnetic resonance (MAS NMR) of ³¹P suggests that metaphosphate or neutral [POO_{3/2}] groups are present in these glasses.

Keywords. EXAFS; MAS NMR; molybdophosphate glasses; tungstophosphate glasses.

1. Introduction

Transition metal oxides WO₃ and MoO₃ do not form glasses even when their melts are quenched at high rates. However they easily form binary glasses over a wide range of compositions in combination with conventional glass forming oxides like B₂O₃ and P₂O₅. Transport, optical, elastic and spectroscopic properties of these glasses have been investigated by a number of workers (Linsey *et al* 1970; Magistris *et al* 1983; Selvaraj and Rao 1985; Bridge and Patel 1986; Kobayashi *et al* 1987; Damodaran and Rao 1989; Chowdari *et al* 1990; Morgan and Magruderh 1990; Gohar 1993; Muthupari and Rao 1994; Muthupari *et al* 1994). In recent years alkali molybdophosphates and alkali tungstophosphate glasses have attracted attention because of their electronic properties and high ionic conductivity. From the studies conducted in this laboratory earlier a model has been proposed for binary MO₃–P₂O₅ (M–Mo or W) glasses in which corner sharing [MO_{6/2}] octahedral and [POO_{3/2}] tetrahedral units (Selvaraj and Rao 1985; Damodaran and Rao 1989) are considered as building blocks of glass structure. The three-dimensional network structure of these glasses is modified by the incorporation of alkali oxides and at high concentration of alkalis, even discrete [MO₄]^{2–} ions are produced (Selvaraj and Rao 1985; Znasik and Jamnicky 1992). It is possible to obtain the local structural information around Mo or W atoms from EXAFS analysis and around P atoms using MAS NMR studies. Even though there are many reports on the thermal, IR, transport, elastic and optical studies, EXAFS (Studer *et al* 1986) and MAS NMR studies are few (Prabakar *et al* 1987). In this paper we report EXAFS and MAS NMR studies on a range of sodium molybdophosphate and sodium tungstophosphate glasses. The structure of the glasses have been discussed in the light of the model proposed for these glasses earlier from this laboratory (Selvaraj and Rao 1985).

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2. Experimental

Sodium molybdophosphate and sodium tungstophosphate glasses of several compositions have been prepared starting from analar grade Na_2CO_3 (BDH), $(\text{NH}_4)_2\text{HPO}_4$ (BDH), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (E-Merck) and WO_3 (Cerac Inc.). Required quantities of the above materials were thoroughly mixed and heated in a platinum crucible to 673 K in an electrically heated muffle furnace for several hours in order to remove H_2O , NH_3 and CO_2 . The samples were then melted and held at temperatures of 1100 K–1500 K for 30 min and quenched between two stainless steel plates. The compositions of the glasses are given in table 1. The glasses are grouped into three series: CM (or CW), CN and MP (or WP) depending on the nature of substitution for convenience. The series CN and CM (or CW) represent compositions where Na_2O and MoO_3 (or WO_3) are kept constant. The MP (or WP) series represents pseudobinary compositions of MoO_3 (or WO_3) and P_2O_5 .

Table 1. Structural parameters derived from Mo-K and W-L_{III} EXAFS of molybdophosphate and tungstophosphate glasses.

Glass number	Composition (mol %)	Coordination no. (<i>N</i>)	<i>r</i> (Å)	$\Delta\sigma^2$
	$\text{Na}_2\text{O} : \text{MoO}_3 : \text{P}_2\text{O}_5$			
CM				
451	40 : 50 : 10	6.1	1.73	0.0006
154	10 : 50 : 40	6.3	1.71	0.0015
CN				
451	40 : 50 : 10	6.1	1.73	0.0006
442	40 : 40 : 20	6.4	1.71	0.0008
424	40 : 20 : 40	6.3	1.71	0.0010
MP				
MP2	— : 80 : 20	6.2	1.71	—
MP4	— : 60 : 40	6.4	1.70	—
	$\text{Na}_2\text{O} : \text{WO}_3 : \text{P}_2\text{O}_5$			
CW				
451	40 : 50 : 10	5.2	1.76	0.0001
		1.0	2.21	0.0001
352	30 : 50 : 20	3.2	1.76	0.0015
		2.8	2.23	0.0015
CN				
451	40 : 50 : 10	5.2	1.76	0.0001
		1.0	2.21	0.0001
442	40 : 40 : 20	3.2	1.73	0.001
		2.8	2.19	0.003
424	40 : 20 : 40	3.1	1.74	0.002
		2.9	2.19	0.002
WP				
WP2	— : 80 : 20	5.7	1.74	0.0005
		0.4	2.17	0.000
WP4	— : 60 : 40	3.1	1.74	0.0013
		2.9	2.17	0.0013

EXAFS associated with K-edge of Mo, Mo-K and L_{III} -edge of W, W- L_{III} were recorded using a Rigaku spectrometer with a rotating anode X-ray generator (Ru-200B, Rigaku, Japan) at room temperature. For Mo K EXAFS, a Ge (440) crystal was used as a monochromator with 0.1 mm slit for X-rays from a Cu target. The spectral resolution is 7 eV at 20 keV incident energy. W L_{III} EXAFS was recorded using a Ge (330) monochromator and Mo target. The slit width used is 0.2 mm. The EXAFS of the glasses were recorded with self supporting thin pellets of glass samples. The thickness of the pellets were adjusted so that the extinction value jumped by a factor of 2 at the absorption edge in all cases. EXAFS of the reference compounds, $CaMoO_4$ and $CaWO_4$, were also recorded under the same conditions. The EXAFS data was treated using a multiphasic model involving additive relationship of EXAFS function (Kulkarni *et al* 1989). The Fourier transforms of EXAFS data were obtained with $k_{min} = 4$ and $k_{max} = 12 \text{ \AA}^{-1}$ for both Mo K and W L_{III} edges after weighing the EXAFS data by k^3 .

^{31}P MAS NMR spectra were recorded using a bruker MSL 300 solid state high resolution spectrometer operating at a 121.495 MHz with a magnetic field of 7.05 Tesla. A 90° pulse with a duration of 5 μsec and a pulse delay of 5 sec was employed. A cylindrical zirconia rotor with a spinning speed of 3000–4000 Hz was used in all experiments. The chemical shift values are given with respect to ^{31}P signals from 85% H_3PO_4 used as a reference material (negative shifts are due to high field).

3. Results and discussion

In these experiments, we have examined the structure around Mo or W using EXAFS while the structure around P were examined using ^{31}P MAS NMR. We discuss below in separate sections the EXAFS and MAS NMR results.

3.1 EXAFS of Mo-K and W- L_{III} absorptions

The Fourier transforms of Mo K edge of the molybdophosphate glasses (the radial distribution functions) are shown in figure 1. The Fourier transforms are similar for all the glasses with a prominent peak at 1.72 $\text{\AA}$ which corresponds to Mo-O distance. Inverse Fourier transforms of the radial distribution functions with various R windows were performed and curve fitted using phase and amplitude parameters obtained from $CaMoO_4$ ($N = 4$ and $r = 1.76 \text{ \AA}$, where N is the coordination number and r the distance between Mo and O atoms). The results are summarized in table 1. Figure 2 shows the Fourier transforms of EXAFS associated with W L_{III} edge in tungstophosphate glasses. The inverse transforms of the radial distribution functions for R windows (1–2 $\text{\AA}$) were carried out employing the phase and amplitude parameters of the W-O in $CaWO_4$ ($N = 4$ and $r = 1.78 \text{ \AA}$). The results are presented in table 1. From figure 1 and table 1, it is evident that the oxygen coordination (N) around Mo and the first neighbour Mo-O distances are nearly identical for all compositions. However, W L_{III} EXAFS results show a slightly different trend. Unlike in the molybdophosphate glasses, the first coordination (W-O) peak exhibits a split feature in several compositions. Splitting indicates the presence of a two-subshell structure of oxygen coordination around tungsten atoms. The distances

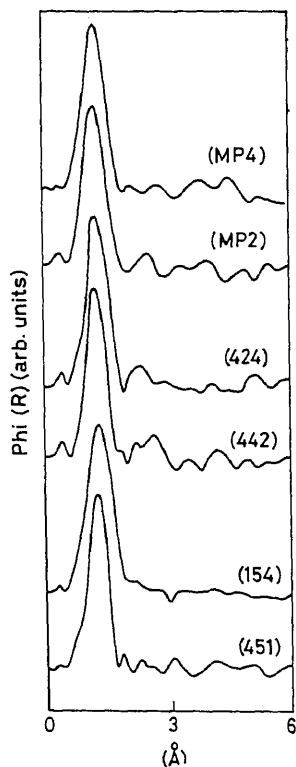


Figure 1. Fourier transforms of the Mo-K EXAFS of molybdophosphate glasses. The glass numbers are indicated in the parenthesis on the right side of each spectrum. (Refer table 1 for compositions).

W-O from the two oxygen subshells are 1.75 and 2.25 Å respectively. Only the low P_2O_5 containing glasses (glasses WP2 and 451) exhibit a single peak nature like in molybdophosphate glasses. But in both molybdophosphate and tungstophosphate glasses, the disorder parameter $\Delta\sigma^2$ increases with P_2O_5 content in all the series except in MP.

From these results, it can be seen that the coordination number of both Mo and W atoms are 6 indicating that these atoms are likely to be present in octahedral positions. Thus it provides strong support to the structural model of molybdophosphate and tungstophosphate glasses proposed earlier from this laboratory. Briefly, according to this structural model, molybdophosphate and tungstophosphate glasses consist of corner sharing $[MO_{6/2}]$ octahedra and $[POO_{3/2}]$ tetrahedra. When alkali oxide is added, the glass network is modified and structural units such as $[MO_{5/2}O]^-$ ($\equiv M_1$), $[MOO_{4/2}]^{2-}$ ($\equiv M_2$), $[POO_{2/2}O]^-$ ($\equiv P_1$) and discrete anions like $[MO_4]^{2-}$ ($\equiv M'_2$) are created. In spite of the lower connectivities of the latter structural entities, the coordination of Mo (or W) remains the same, i.e. 6, except in discrete anions, M'_2 . This is clearly borne out from the present studies of Mo-K and W-L_{III} EXAFS. However the presence of two-oxygen subshell structure in high P_2O_5 containing tungstate glasses with two W-O nearest neighbour distances of 1.75 Å and 2.20 Å respectively is a reflection of the tetrahedral distortion of $[WO_6]$ octahedra resulting

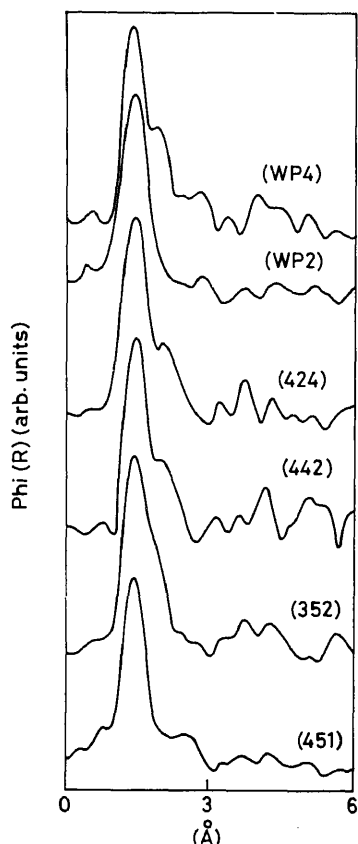
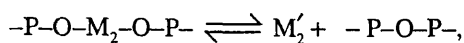


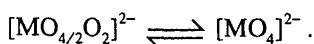
Figure 2. Fourier transforms of the W L_{III} EXAFS of tungstophosphate glasses. (Refer table 1 for compositions).

in two different W–O bond lengths. Pulsed neutron studies on alkali tungstate glasses and IR studies on tungstophosphate glasses have also shown that (Selvaraj and Rao 1985; Kobayashi *et al* 1987) two different W–O bond lengths are present in the glass network.

In the highly modified, high P₂O₅ containing glasses the following bond switching reaction is envisaged in the model.



or equivalently,



The M₂ → M'₂ conversion is expected to be aided by both higher concentration of alkalis and presence of more –P–O–P– linkages. In such glasses (for e.g. glasses CN433 and CN424 in table 2), one can expect the presence of M'₂ units. Both elastic properties and infrared spectroscopic studies indicate the presence of M'₂

Table 2. ^{31}P MAS NMR data of molybdophosphate and tungstophosphate glasses.

Molybdate glasses			Tungstate glasses		
Glass no.	δ (ppm)	FWHM (ppm)	Glass no.	δ (ppm)	FWHM (ppm)
CM			CW		
451	6.6	10.5	451	8.91	9.2
352	1.1	11.9	352	9.0	18.3
253	-6.6	16.4	253	12.7	24.8
154	-15.5	20.9	154	14.9	29.5
CN			CN		
451	6.6	10.5	451	8.9	9.2
442	4.7	13.4	442	9.3	10.9
433	-3.7	14.9	433	11.9	12.2
424	-6, -17.8	-	424	-8, -17.8	-
MP			WP		
MP2	-9.2	12.7	-	-	-
MP3	-10.8	22.3	WP3	-12.0	9.7
MP4	-15.4	26.8	WP4	-13.5	11.9
MP5	-17.3	-	WP5	-13.5	12.3

type of structural units along with other units such as M_1 , M_2 and P_1 in the highly modified high P_2O_5 glasses (Selvaraj and Rao 1985; Damodaran and Rao 1989; Muthupari *et al.*, unpublished results). In EXAFS we should expect the formation of M'_2 units to be reflected in a slight decrease of average coordination number only. However the uncertainties ($\pm 10\%$) in the determination of N prevents clear identification of the presence of M'_2 units in the dominating concentration of other units possessing coordination of six oxygens.

3.2 ^{31}P MAS NMR studies

Typical ^{31}P MAS NMR spectra of molybdophosphate and tungstophosphate glasses are shown in figure 3. The chemical shifts and the full width at half maxima (FWHM) obtained from these spectra for all the glasses are given in table 2. All the glasses exhibit a single resonance peak except the glass 424, which exhibits two resonance peaks. In all the series, with increasing P_2O_5 content, the chemical shifts shift to lower values. FWHM values are indicative of the extent of disorder in the material. FWHM values almost uniformly increase with increasing P_2O_5 in both molybdophosphate and tungstophosphate glasses suggesting that greater disorder is introduced into the glass structure when the P_2O_5 content is increased. This increase in the disorder may be attributed to two reasons: (i) alterations of the chemical nature of the tetrahedra around phosphorous due to the formation of P_1 units and (ii) the increased complexity of the second neighbour environment of phosphorous due to the formation of units like M_1 , M_2 and M'_2 . In simple binary MP and WP glasses it is clearly due to the variation in the number of $[\text{MO}_{6/2}]$ and $[\text{POO}_{3/2}]$ units surrounding any $[\text{POO}_{3/2}]$ units. The flexibility of P-O-P angles being higher than P-O-M angles (M is in an octahedron) and produces a greater

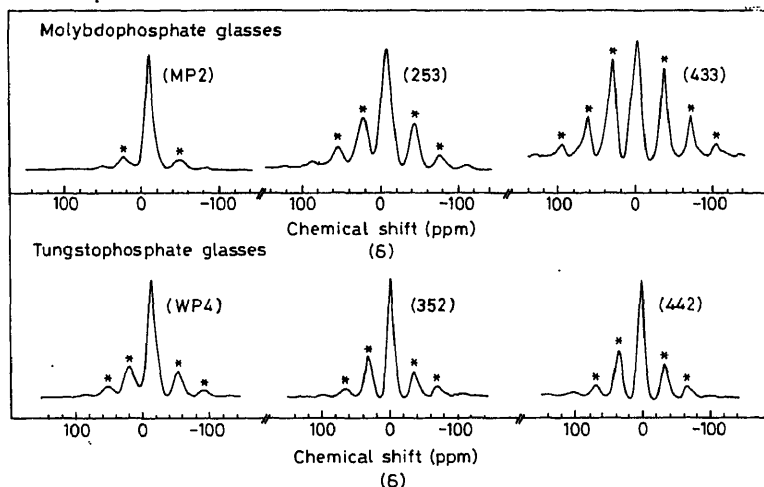
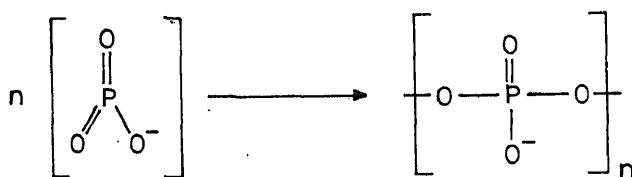


Figure 3. Typical ^{31}P MAS NMR spectra of few molybdophosphate and tungstophosphate glasses. Spinning side bands are marked with asterisks. The compositions are identified by their respective numbers in table 2.

spread of second neighbour environment in P_2O_5 rich glasses. Correspondingly $\Delta\sigma^2$, disorder parameter is high in high P_2O_5 containing glasses.

In an earlier MAS NMR investigation (Prabakar *et al* 1987) on phosphate glasses, it was shown that the dominant species in the phosphate glasses is always the metaphosphate units, because these polymerize to give rise to chains.



Correspondingly the MAS NMR signal from all phosphate glasses (Prabakar *et al* 1987) generally fall into a separate phase field characterized by a parameter, $(Z_{\text{eff}}/r) \times q > 0$ on the abscissa and ^{31}P chemical shifts values generally < 20 ppm. Here, Z_{eff} represents the charge on the cation wherever it is present; otherwise it refers to the partial charge on the molybdenum or tungsten, r is the ionic radius of the cation (referred to the most common coordination number) and q the partial charge on the phosphorous atom calculated using the Sanderson's procedure (Sanderson 1983). The parameter has the units of energy. In figure 4, the phase field is reproduced from our earlier work (Prabakar *et al* 1987) and the data pertaining to the present glasses are marked which provides additional evidence to the presence of only P or P_1 units in the glasses.

It was mentioned earlier that $[\text{MO}_{6/2}]$ octahedra and $[\text{POO}_{3/2}]$ tetrahedra are corner connected in the formation of these glass structures. Further the model also assumes that the network is chemically ordered, i.e. like unit connections (M-M or P-P)

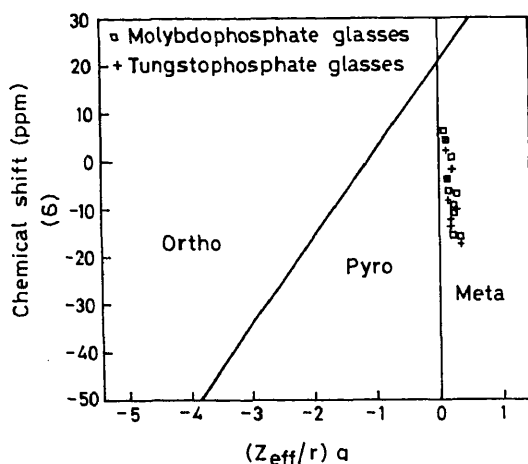


Figure 4. Plot of ^{31}P chemical shifts of molybdophosphate and tungstophosphate glasses vs $(Z_{\text{eff}}/r) \times q$.

Table 3. Mole fractions of different kinds of structural species present in the glasses. (In fractions; alkali fractions not included).

Glass no.	Species				
	M	M ₁	M ₂	P	P ₁
154	0.277	—	0.0692	0.554	—
253	0.218	—	0.145	0.436	—
352	0.156	—	0.233	0.311	—
451	0.085	—	0.343	0.172	—
442	—	0.15	0.15	0.15	0.15
433	—	0.133	0.066	0.133	0.266
424	—	—	0.12	0.24	0.24
MP2	0.66	—	—	0.34	—
MP3	0.538	—	—	0.462	—
MP4	0.482	—	—	0.572	—

Where M = $[\text{MO}_6]^{2-}$; M₁ = $[\text{MO}_5\text{O}]^{2-}$; M₂ = $[\text{MO}_4\text{O}_2]^{2-}$;
P = $[\text{POO}_{3/2}]$; P₁ = $[\text{POO}_{2/2}\text{O}]^{2-}$

of such network by an alkali oxide occurs by hierarchical bond breaking in the order of their bond energies of linkages, $E_{\text{MOM}} < E_{\text{MOP}} < E_{\text{POP}}$. Hence the MOM linkage will be modified first, and then MOP and finally the POP linkage will be modified (Selvaraj and Rao 1985). In fact this is well supported from a consideration of partial charges calculated on the basis of molecular electronegativities as shown elsewhere (Muthupari *et al*, unpublished results). Using such hierarchical bond breaking order, different structural results such as M₁, M₂ and P₁ are evaluated in such glasses and listed in table 3.

From table 3, it can be seen that the glasses studied contain neither ortho nor pyrophosphate units but only either neutral $[\text{POO}_{3/2}]$ or metaphosphate groups. Table 3 also confirms that $[\text{MO}_{6/2}]$, M₁ and M₂ units dominate the structure and any

M_2' units formed can only be in low concentrations and therefore not observed in EXAFS.

4. Conclusions

EXAFS and MAS NMR studies on the sodium molybdophosphate and sodium tungstophosphate glasses reveal that the structure is made up of $[MO_{6/2}]$ octahedra and $[POO_{3/2}]$ tetrahedra which are modified by the addition of alkali oxide. EXAFS results show that both the transition metal atoms (Mo and W) are present in 6 coordinated environment. MAS NMR results indicate the presence of metaphosphate or neutral $[POO_{3/2}]$ groups in the glass network.

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Growth, characterization and electrical anisotropy in GaTe—a natural semiconducting superlattice

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Abstract. GaTe is a III–VI semiconductor which has layered structure with large anisotropy in electrical properties. Growth of single crystals by the Bridgman technique permitted the measurement of thermoelectric power in orthogonal directions from which the anisotropy of hole effective masses were determined for the first time. From resistivity and Hall effect measurements the carrier activation energies and scattering mechanisms between 10–300°K were found.

Study of the temperature dependence of conductivity revealed a variety of conduction mechanisms including weak localization below 20°K, hopping conduction between 20–50 K and band conduction in and across the layer planes at $T > 70$ K. Weak localization was confirmed through observation of negative magnetoresistance. The I – V characteristics showed quantized behaviour due to tunneling across potential barriers, which may be due to stacking faults between layer planes as observed by TEM studies.

Keywords. GaTe; III–VI semiconductor; electrical anisotropy.

1. Introduction

GaTe crystallizes in the monoclinic system (space group C_2^2). According to the Mooser–Pearson criterion it is a III–VI semiconductor having one cation–cation (M–M) bond and forms X–M–M–X chains. There is strong covalent bonding within the layer planes with weak van der Waals bonding between them resulting in easy cleavage. Due to difficulties in crystal growth only the in-plane properties have been reported by Fischer and Brebner (1962), Manfredotti *et al* (1975) and Segura *et al* (1989). The subject has been reviewed by Fivaz and Schmid (1976).

In the present work high quality crystals of InTe and GaTe were grown by the Bridgman technique using very slow growth rates after synthesis from the elements. The crystals were characterized by Laue back reflection and electron diffraction for structure followed by energy dispersive X-ray analysis (EDAX) and X-ray photoelectron spectroscopy (XPS) to establish stoichiometry. Impurity analysis was carried out using inductively coupled plasma emission (ICP). The optical band-gap at 300 K was found to be 1.66 eV and direct in nature. Detailed studies of the electrical transport properties between 10–350°K were thereafter carried out as will be described in this paper. The study of deep levels in orthogonal directions in GaTe has already been reported by Pal *et al* (1994). A new semiconducting ferroelectric has also been found in the related $\text{Ge}_{1-x}\text{Ga}_x\text{Te}$ system by Bose and Pal (1994).

2. Crystal growth

Ga and Te of 6Ns purity were used for synthesis of the compound in sealed quartz

tubes using prolonged and continuous rotation for homogenization. The material was then placed in a conically-tipped ampule in a 3-zone vertical furnace and heated to temperatures well above the melting point of 1097 K. The charge was lowered at 1–1.2 mm/h. A short post-growth anneal at 100–120°C was carried out to give the desired monoclinic phase. The resulting ingots were 1.25 cm in diameter and 2.5 cm in length (Pal *et al* 1994) and could be cleaved easily parallel to the layer planes.

3. Characterization

X-ray powder diffraction studies were carried out which confirmed the monoclinic structure of GaTe with unit cell parameters $a = 17.32$ Å, $b = 4.05$ Å and $c = 10.59$ Å with $\beta = 104.4^\circ$. This corresponded to Ga–Ga and Ga–Te bond lengths of 2.473 and 2.638 Å respectively and Te–Te distance of 4.096 Å. Laue back-reflection showed that the (001) direction was along the layer plane. Electron diffraction studies using a Philips transmission electron microscope (TEM) at 100 keV were also carried out. The diffraction pattern showed the expected 2-fold symmetry and confirmed the values of the lattice parameters. Electron micrographs showed the presence of dislocations in the basal plane and ribbons of stacking faults similar to those in GaSe.

The Ga : Te ratio determined by EDAX and XPS are compared in table 1 which shows reasonable agreement between the bulk and surface.

ICP analysis was conducted on the elements as well as the compound after crystal growth. The principal impurities at trace levels were found to be Pb (0.67 ppm), Sn (0.56 ppm), Fe (0.34 ppm) and Mg (0.26 ppm), the first originating from Ga and the others from Te.

4. Optical absorption

Thin platelets were cleaved from the crystals and polished to mirror finish. The optical absorption was studied perpendicular to the layer plane at 300 K using a UV 365 Shimadzu spectrophotometer. The absorption plotted as $(\alpha h\nu)^2$ vs $h\nu$ gave a straight line indicating a direct gap of 1.66 ± 0.002 eV in good agreement with a value of 1.663 eV reported by Brebner and Fischer (1962).

5. Thermoelectric power (TEP)

TEP was measured between 140 and 300 K maintaining a constant temperature

Table 1. Compositional analysis of GaTe single crystals.

	Ga (at %)	Te (at %)
EDAX	49.2–49.3	50.8–50.7
XPS	49.1–49.2	50.9–50.8

difference of 7–8°C between the ends of the samples aligned along or perpendicular to the layer planes. The sign of the TEP was always positive indicating hole conduction. The nature of variation for the two cases is shown in figure 1. At 300 K the TEP in the layer plane was 873 $\mu\text{V/K}$ which increased to 1200 $\mu\text{V/K}$ at 140 K. In the perpendicular direction at 300 K TEP was 1233 $\mu\text{V/K}$, went through a minimum and thereafter increased to 1550 $\mu\text{V/K}$ at 140 K. The activation energies in two temperature regions given in table 2 were in good agreement with the results of Hall effect measurements. The decrease in TEP with increase in temperature is essentially due to the increase in hole concentration i.e. the Fermi level moves towards the valence band in this temperature range and hence $E_F - E_V$ in (1) decreases.

TEP is related to the Fermi level in a *p*-type semiconductor by

$$S = + \frac{k}{e} \left[\frac{E_F - E_V}{kT} + A + \frac{5}{2} \right], \quad (1)$$

where *A* is a constant whose value depends on the scattering mechanism being 3/2, -1/2 or +1/2 for impurity, acoustical phonon or optical phonon scattering respectively. For GaTe along the layer planes between 140–300 K, *A* = +1/2

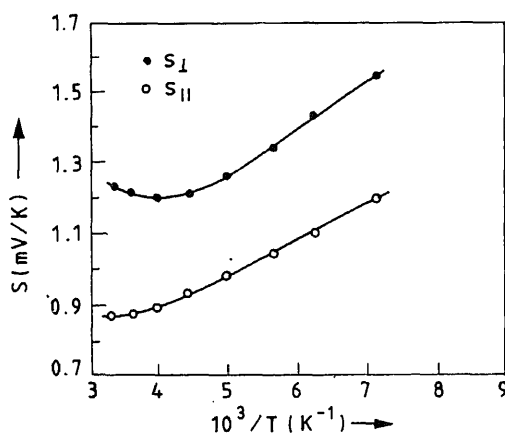


Figure 1. Temperature dependence of thermoelectric power *S* for *p*-GaTe parallel and perpendicular to layer plane.

Table 2. Activation energies and hole effective masses in GaTe from TEP studies.

Orientation	E_a (meV) (80–100 K)	E_a (meV) (100–250 K)	m_h^*	<i>A</i>
Parallel to layer plane	22.5	73.6	0.465 m_0 (± 0.01)	+0.5
Perpendicular to layer plane	39.7	111.0	0.995 m_0 (± 0.01)	+4.5

indicating optical phonon scattering whereas in the perpendicular direction $A = 4.5$ in the same temperature range. This cannot be explained by any of the above scattering mechanisms and may be due to the existence of planar defects between the layers. The hole effective masses were calculated from the values of N_v in the two directions and were found to be $0.465 m_0$ and $0.995 m_0$ respectively as given in table 2.

6. Resistivity and Hall effect

The resistivity of samples were measured both along and perpendicular to the layer planes by the van der Pauw method. Ohmic contacts were made by indium evaporation followed by annealing at 200°C in Argon atmosphere for 5 min. Hall effect measurements were carried out between 77–300 K at magnetic fields up to 0.5 T. Arrhenius plots of $\ln \sigma$ and $\ln \sigma$ vs $1/T$ are shown in figure 2. Two sets of activation energies were obtained from the graphs in each direction between 80 and 100 K and 100 and 250 K. The values along the layer planes were 0.023 eV and 0.074 eV respectively lower than the corresponding values 0.040 eV and 0.110 eV in the perpendicular direction. In general $\sigma_{\parallel} \gg \sigma_{\perp}$ as expected for layered compounds the ratio known as the anisotropy factor being given by

$$\sigma_{\parallel} / \sigma_{\perp} = A \exp (\Delta E / kT) = m_{\perp}^* / m_{\parallel}^* \exp (\Delta E / kT), \quad (2)$$

where $m_{\perp}^*$ and $m_{\parallel}^*$ are the effective masses. The value of ΔE was found experimentally to be 0.04 eV between 182 and 30 K and shows the effect of defects on $\sigma_{\perp}$.

Figure 3 shows the variation of hole mobility with temperature in the two directions between 80 and 300 K with $p = (2.75-6.5) \times 10^{15}/\text{cm}^3$. At 300 K $\mu_{\parallel} = 25-40 \text{ cm}^2/\text{Vsec}$ and $\mu_{\perp} = 10-15 \text{ cm}^2/\text{Vsec}$ while near 80 K these values increased to $450-500 \text{ cm}^2/\text{Vsec}$ and $100-110 \text{ cm}^2/\text{Vsec}$ respectively. These are much

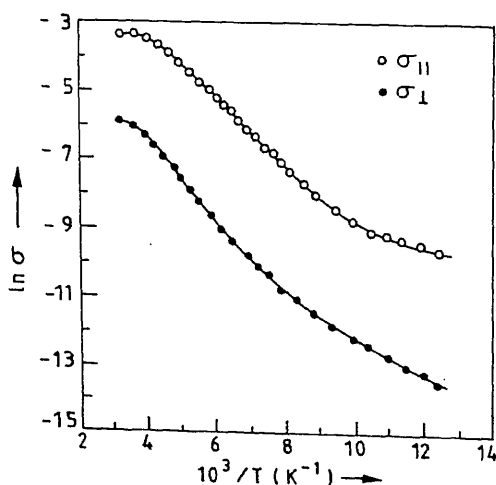


Figure 2. Temperature dependence of conductivity in p -GaTe measured parallel and perpendicular to the layer plane.

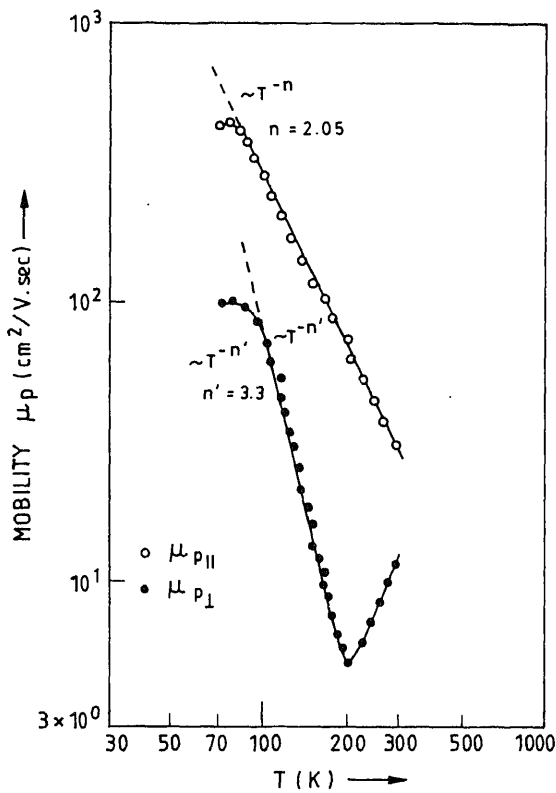


Figure 3. Variation of hole mobility with temperature in two directions ($\log \mu$ vs $\log T$).

higher than the highest mobility of $\mu_{||} = 150 \text{ cm}^2/\text{Vsec}$ reported by Augelli *et al* (1977) attesting to the high quality of the present crystals. The hole mobility had a temperature dependence for $T > 100 \text{ K}$ given by T^{-n} where $n = 2.05$ parallel to and 3.3 perpendicular to the layer plane.

The temperature dependence of $\mu_{||}$ has been explained by Fivaz and Schmid (1976) as due to scattering by homopolar optical phonons polarized parallel to the layer planes. Good agreement with this theory was obtained assuming interaction with an optical phonon of energy $\hbar\omega = 0.014 \text{ eV}$ which was observed in Raman studies by Cerdeira *et al* (1977). If the carrier-lattice coupling constant $g^2 = 0.31$ as estimated by Camassel *et al* (1977), the in-plane effective mass $m^* = 0.47 m_0$ is in excellent agreement with TEP results. The hole density-of-states effective mass was estimated by Manfredotti *et al* (1975) to be $0.6 m_0$. From this the effective mass perpendicular to the layer planes is found to be $1.0 m_0$, again in good agreement with the value of $0.995 m_0$ obtained from TEP (table 2).

The Hall mobility $\mu_{\perp}$ showed a minimum with a thermally activated behaviour for $T > 200 \text{ K}$ with $\Delta E = 0.040 \text{ eV}$ as observed in the case of the conductivity anisotropy. Similar behaviour has been observed in GaSe and is attributed to the presence of interlayer stacking faults.

Weak localization in InSe has been reported by El-Khatouri *et al* (1989) who examined conductivity variation with temperature but only along the layer planes. Conductivity studies were thus carried out for GaTe between 10–50 K in a closed cycle He cryostat with the electric field parallel or perpendicular to the layer planes. Results are given in figures 4a and b and summed up in table 3.

It is seen (figure 4a) that parallel to the layer plane weak localization occurs for $T < 20$ K the relation followed being given by (Lee and Ramakrishnan 1985),

$$\Delta G = (\lambda e^2 / \hbar^2) \ln T, \quad (3)$$

where $\lambda = \alpha p^2 / 2\pi^2$. From experiment $\lambda = 0.051$ giving $p = 1$ for a non-interacting electron gas with $\alpha = 1$. The value of $(e^2 / 2\pi^2 \hbar)$ was found from the slope to be 1.23×10^{-5} mhos.

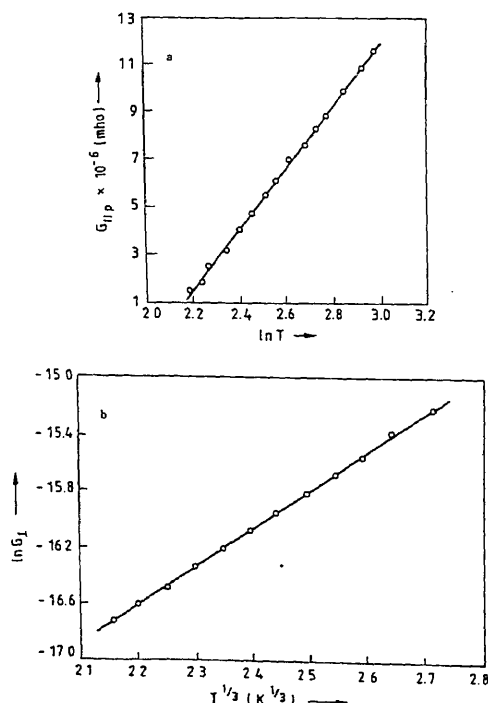


Figure 4. a. Conductance G vs $\ln T$ along the layer planes for $T = 9$ –20 K and b. conductance $\ln G$ vs $T^{1/3}$ perpendicular to the layer planes for $T = 9$ –20 K.

Table 3. Conductivity variation of GaTe in orthogonal directions.

Direction	$T = 9$ –20 K	$T = 20$ –50 K
Parallel to layer plane	$G \propto \ln T$	$\sigma \propto T^{1/2}$
Perpendicular to plane	$G \propto \exp(T/T_0)^{1/3}$	$\sigma \propto \exp(T/T_0)^{1/4}$

For $T=20\text{--}50\text{ K}$ the $T^{1/2}$ variation is a consequence of 3-dimensional conduction under weak localization which is proportional to $T^{p/2}$, where $p=1$ in the present case.

In the perpendicular direction the temperature variation (figure 4b) is characteristic of 2-D hopping for $T < 20\text{ K}$ with dimensional crossover to 3-D Mott-type hopping for $T > 20\text{ K}$. These results have been discussed in detail by Basak (1994).

The two-dimensional nature of conduction parallel to the layer planes resulted in negative longitudinal magnetoresistance (positive magnetoconductance) being observed at low temperatures with relatively weak fields $< 0.4\text{ T}$. The results are depicted in figure 5a and summarized in table 4. At 10 K the application of magnetic field results in suppression of weak localization and hence increase in conductance which is proportional to H^2 (figure 5b). At $T = 80\text{ K}$ for band conduction, increase in scattering and decrease in hole mean-free-path due to the applied magnetic field results in positive magnetoresistance as expected.

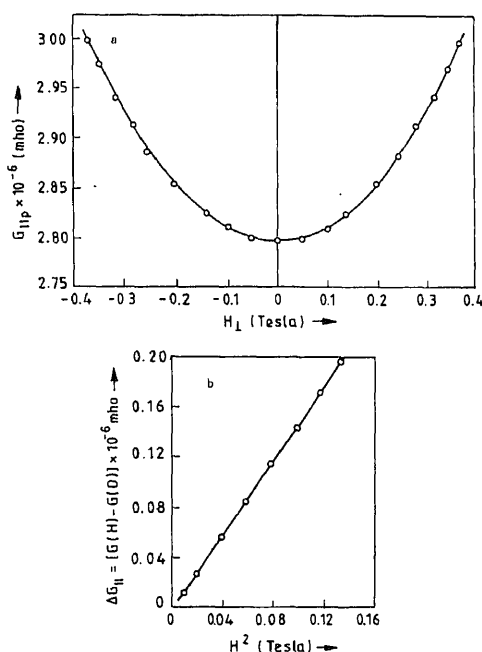


Figure 5. a. Transverse magnetoconductance in the layer plane at $T = 10\text{ K}$ and b. change in conductance ΔG vs H^2 at $T = 10\text{ K}$.

Table 4. Magnetoresistance in GaTe.

Direction	$(\Delta\rho/\rho)\text{ (%)}$	
	$T = 10\text{ K}$	$T = 80\text{ K}$
Parallel to layers	-7.14%	+ 11.5%
Perpendicular to layers	-5.18%	+ 8.3%

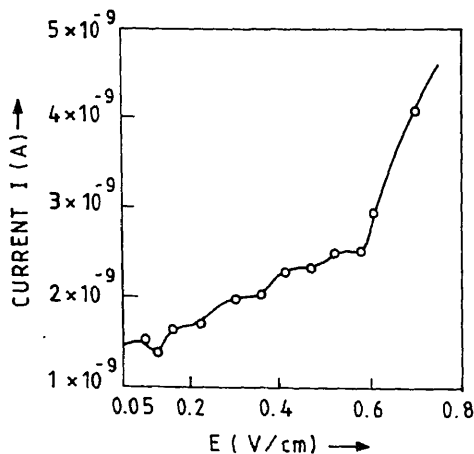


Figure 6. I - V characteristic across the layer plane at $T = 10$ K.

8. I - V characteristics

The I - V characteristics of the samples were studied at 10–25 K at low electric fields both in and across the layer planes. In the latter case it was found that I showed an initial decrease indicating negative differential resistance (NDR) and then increased in discrete steps at 10 K (figure 6), the effect vanishing at 25 K. This behaviour is similar to the resonant tunneling (RT) observed in MBE grown GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ superlattices at 77 K and 300 K by Morkoc *et al* (1986) which also showed NDR. Resonant tunneling of holes, as in the present case, was observed in AlAs/GaAs quantum well structures by Mendez *et al* (1985). RT is due to the applied bias bringing successive quasi-bound states in the narrow regions confined by the potential barriers into alignment permitting tunneling and resulting in the observed current steps. At $T > 20$ K thermal excitation over the potential barriers becomes possible while at higher fields field-assisted tunneling takes over. In the GaAs/AlAs system the confining potential for holes is ~ 150 meV and well widths are typically less than 10 nm which gives large separation between the quantized levels. Hence NDR can be observed at 300 K. For GaTe the confining potentials due to stacking faults are estimated to be a few meV and potential wells are much wider so that the phenomenon is only observed at $T < 10$ K. This is to the authors knowledge the first report of such an observation in a natural superlattice.

9. Conclusion

The study of anisotropy of the transport properties of the layered chalcogenide GaTe revealed novel phenomena which can be explained on the basis of weak localization at low temperatures and its removal due to applied magnetic field resulting in negative magnetoresistance. The anisotropy of effective mass in orthogonal directions was determined from TEP studies while the temperature dependence of mobility μ_H indicated homopolar optical scattering. Resonant tunneling with NDR was observed in such a natural superlattice for the first time.

Acknowledgement

One of the authors (SP) is grateful to the University Grants Commission for the award of a Fellowship.

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Successively pulse plated cadmium selenide films and their photoelectrochemical behaviour

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Abstract. In successive pulse plating, the pulse deposition is repeated after a definite duration of plating preceded by a mild cleaning of the electrode and with a fresh deposition bath for the same duration. In this study, CdSe films were deposited on Ti substrates by successive pulse plating from a bath containing CdSO_4 and SeO_2 at a current density of 80 mA cm^{-2} and a duty cycle of 3.3% for a duration of 30 min. The films heat-treated to 550°C for 20 min in argon atmosphere, were polycrystalline with a hexagonal structure. At an illumination of 60 mW cm^{-2} , a conversion efficiency of 4.5% for the photoetched film and 1.7% for the chemically etched one were determined.

Keywords. Cadmium selenide; pulse plating.

1. Introduction

n-CdSe has been used as a photoanode in photoelectrochemical (PEC) cells to give a high power conversion efficiency, both in single crystal and polycrystalline forms. In recent years, there has been considerable work in the study of polycrystalline electrodes for PEC cells, since 70% of the single crystal efficiency can be obtained with low cost polycrystalline films. Vacuum evaporation, spray pyrolysis, chemical bath deposition, slurry coating, electrodeposition etc have been employed earlier for the preparation of these films. We report here the results on successively pulse plated CdSe films.

Metal deposits obtained by pulse plating show distinct advantages like improved deposit distribution, adhesion and lower impurity content compared to conventional dc electrodeposition. The properties of the deposit can be varied by varying the current density and duty cycle. Higher nucleation rates are possible with pulse plating (Rehrig *et al* 1977; Popov *et al* 1980; Lam *et al* 1983). Crack-free hard deposits with low porosity and low internal stress are obtainable with pulsing (Devaraj *et al* 1989a, b). An increased average grain size and uniform grain distribution (compared to conventional electrodeposition) are noticed in pulse plated films.

The main purpose of carrying out successive pulse plating (pulse deposition repeated after a definite duration of plating preceded by a mild cleaning of the electrode and with a fresh deposition bath for the same duration) is to obtain higher film thicknesses which, in turn will yield higher grain size (Saitoh *et al* 1976) due to better nucleation sites, yielding higher conversion efficiencies (Lanza and Hovel 1980; Pandey *et al* 1991) for photoelectrochemical cells.

This paper reports the comparative PEC results obtained with successively pulse plated CdSe films with those obtained by conventional pulse plating. The improvements in the output parameters have justified the expectations.

2. Experimental

CdSe films (3 μm thick) were pulse plated cathodically at room temperature on Ti substrates employing a bath of 0.5 M CdSO_4 and 0.005 M SeO_2 which was kept stirred. Graphite was used as the other electrode with an inter-electrode distance of 2 cm. A current density of 80 mA cm^{-2} was employed with an on-time of 1 sec and off-time of 29 sec making the duty cycle 3.3%. Then, the substrates along with the deposited films were taken out, washed well with triple distilled water and introduced in a fresh bath solution of the same composition for a second pulse deposition (which we call successive pulse plating). The other parameters such as current density, duty cycle etc were kept constant for the successive pulse deposition and repeated for the same duration of 30 min. The thickness of the films were found to be 5 μm .

The films were heat treated at 550°C for a duration of 20 min in argon atmosphere, and characterized by X-ray diffraction using CuK_α radiation. Optical absorption studies were carried out employing a Hitachi U 3400 UV-VIS-NIR spectrophotometer. Surface morphology was examined by 35 CF JEOL scanning electron microscope.

The PEC cell consisted of the photoelectrode and a graphite counter electrode with 1 M alkaline polysulphide as the electrolyte. The light source was an Oriel 250 W tungsten halogen lamp. The photon flux reaching the electrode surface was measured by a CEL Suryamapi. After heat treatment, the electrodes were etched chemically in 1 : 3 HCl for 5 sec and rinsed in triple distilled water. Photoetching was performed by shorting the photoelectrode and the counter electrode in 1 : 3 HCl for different durations in the range of 5 to 60 sec under an illumination of 60 mW cm^{-2} . $C-V$ measurements were carried out in polysulphide electrolyte using an EG and G PARC impedance system at different frequencies. Quantum efficiencies at different wavelengths in the range 550–820 nm were measured employing an Applied Photophysics f/3.4 monochromator with a resolution of 0.2 nm.

3. Results and discussion

The X-ray diffraction pattern of a successively pulse plated film is shown in figure 1. The diffractograms indicate the polycrystalline nature of the film with all the major peaks corresponding to hexagonal CdSe. Peaks corresponding to elemental Se or Cd are not present. Surface morphology of the films indicate an average grain size of 3 μm . The grain size is found to increase from 1 to 3 μm after successive pulse deposition.

The power output characteristics of the PEC cells employing the regular pulse deposited and successively deposited films are shown in figure 2. While for the regular pulse deposited films, a V_{oc} of 435 mV, J_{sc} of 3.2 mA cm^{-2} , fill factor (FF) of 0.43 and efficiency (η) of 1% are obtained, for the successively pulse plated films a V_{oc} of 450 mV, J_{sc} of 5 mA cm^{-2} , FF of 0.46 and η of 1.7% are obtained. From the $I-V$ curves, series resistance (R_s) values of 58 ohms and 40 ohms and shunt resistance (R_{sh}) values of 1.66 kohms and 3 kohms have been obtained for the two cases respectively. The enhanced output for the successively pulse plated films is due to their increased grain size. After a 60 sec photoetch of the successively pulse plated films, the output parameters are: V_{oc} = 475 mV, J_{sc} = 11.7 mA cm^{-2} , FF

$\eta = 0.48$ and $\eta_i = 4.8\%$. The cell shows an R_s of 18 ohms and $\ln(10)$ R_{sh} of 5.5 kohms. For the present study, a large number of films [50] had been prepared. The variation in efficiency among the cells was from 4.5% to 4.8%. Other measurements carried out on the successively pulse plated films are V_{fb} , quantum efficiency, minority carrier diffusion length, diffusion layer width and the conductivity.

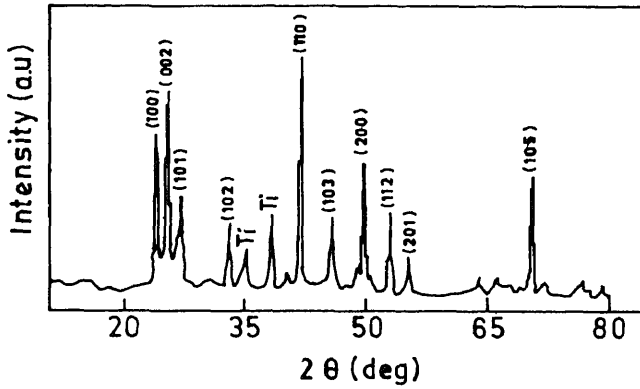


Figure 1. X-ray diffraction pattern of the CdSe film.

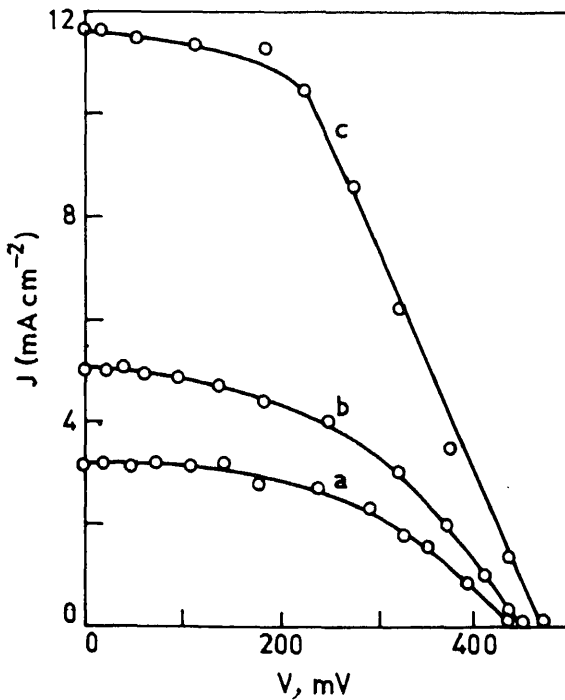


Figure 2. Power output characteristics of the CdSe film. a. single pulse deposited, b. successive pulse deposited and c. after photoetching.

Mott-Schottky plot for a frequency of 10 kHz in 1 M polysulphide electrolyte is shown in figure 3. The linearity of the plot suggests that the impurities are uniformly ionized (Ramprakash *et al* 1988). From the extrapolated intercept on Y-axis, a flat band potential (V_{fb}) of +1.19 V vs SCE was obtained. The plot indicates *p*-type behaviour for the films. *p*-type behaviour has also been reported by Hodes *et al* (1992) for the quantum box CdSe semiconducting films and the reason for the *p*-type behaviour has not been well understood. From the slope of the plot, a value of $5.65 \times 10^{16} \text{ cm}^{-3}$ has been deduced for the carrier density.

Quantum efficiency (ϕ) was evaluated from the spectral response measurements by employing the following expression (Segui *et al* 1991)

$$\phi = \frac{1240 J_{sc}}{\lambda P}, \quad (1)$$

where J_{sc} is current density expressed in A cm^{-2} ; λ the wavelength expressed in nm and P the radiant power absorbed in the photoactive region, expressed in W cm^{-2} . Figure 4 shows the variation of quantum efficiency in the wavelength range 550–820 nm.

A peak quantum efficiency of 0.61 is observed in the region 650–700 nm, agreeing with the band gap of the material.

From Gartner's photocurrent equation for a metal–semiconductor junction, quantum efficiency, ϕ , (Russak *et al* 1980) follows the relation

$$\phi = 1 - (e^{-\alpha W} / 1 + \alpha L_p), \quad (2)$$

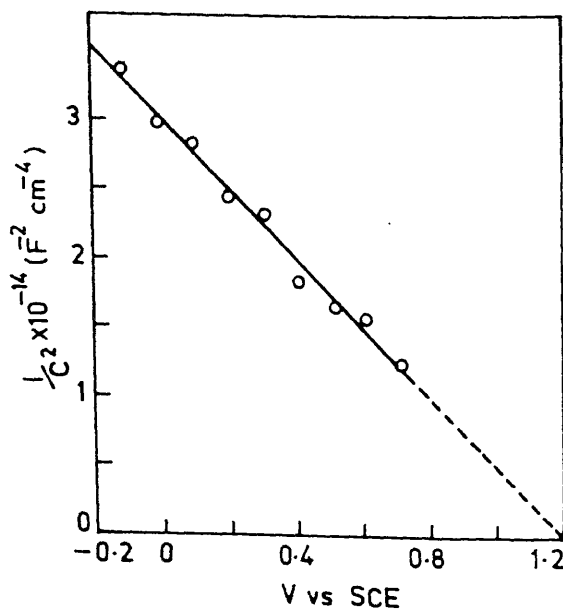


Figure 3. Mott-Schottky plot of successively pulse plated CdSe film in 1 M polysulphide at 10 kHz.

where W is the depletion layer width given by

$$W = [(2\epsilon\epsilon_0/qN_D) (V - V_{fb})]^{1/2}, \quad (3)$$

q is the electron charge, α the absorption coefficient, L_p the diffusion length of the minority carriers, ϵ the dielectric constant of the semiconductor, ϵ_0 the permittivity of free space, V the electrode potential, V_{fb} the flat band potential and N_D the doping density. By choosing a wavelength of relatively weak absorption so that $\alpha L_p \ll 1$ and $W \ll 1$ (Pandey *et al* 1991), the following relationship is obtained

$$\phi = L_p.$$

Hence

$$\phi^{-1} = (L_p)^{-1}.$$

A plot of ϕ^{-1} vs α^{-1} is shown in figure 5. L_p is obtained from the inverse of the slope and is found to be $0.98 \mu\text{m}$. This value of L_p is in close agreement with the value of $0.8 \mu\text{m}$ reported (Russak *et al* 1980) for a CdSe film obtained by the dc electrodeposition technique.

In order to obtain W , (2) can be rearranged as

$$W = -\ln [(1 - \phi) (1 + \alpha L_p)] / \alpha \quad (4)$$

Substituting the corresponding values of α and ϕ when $W \ll 1$, we obtain $W = 0.3 \mu\text{m}$. The maximum reported value (Gutierrez and Salvador 1987) of W for CdSe films is $0.7 \mu\text{m}$. The reported conversion efficiencies are 11.7% for a PEC cell

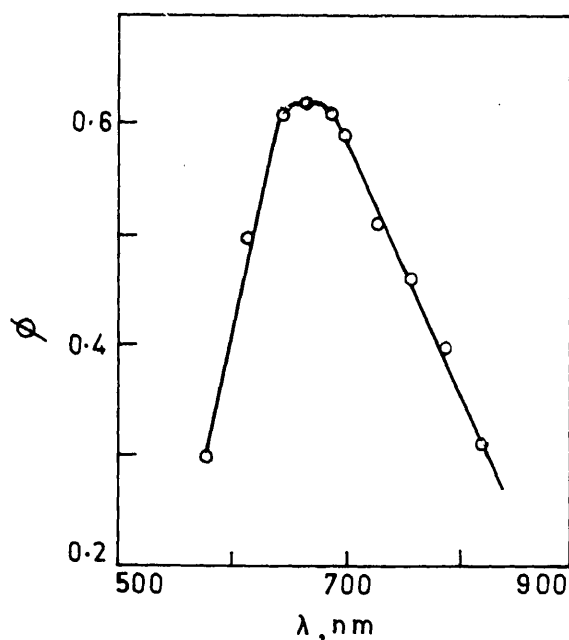


Figure 4. Variation of quantum efficiency (ϕ) with wavelength (λ) for the PEC cell employing successively pulse plated CdSe films.

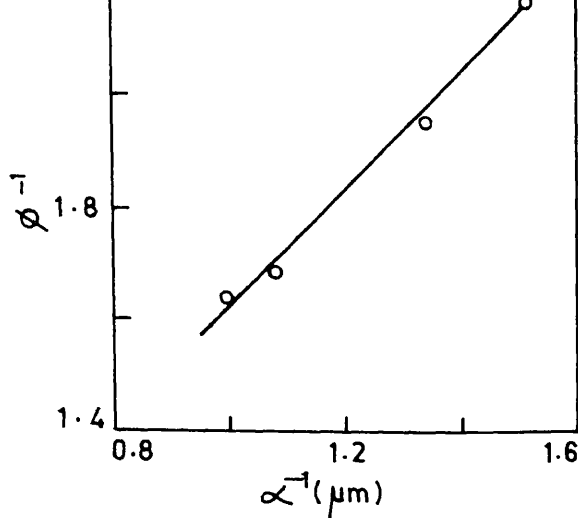


Figure 5. Variation of inverse quantum efficiency (ϕ^{-1}) with reciprocal of absorption coefficient (α^{-1}) for the PEC cell.

with a chemically deposited polycrystalline CdSe film (Savadogo and Mandal 1992) with surface modification and 7.3% with the film obtained by the dc electrodeposition technique (Szabo and Cocivera 1986) and 7.4% with the films obtained by brush plating technique (Murali *et al* 1994).

From the measurement of cross-plane resistance of the CdSe film, the conductivity has been found to be $0.02 \text{ ohm}^{-1} \text{ cm}^{-1}$. Employing the values of N_D , the mobility of the electrons is found to be $2.4 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$. This value is in agreement within the range of values reported (Wynands and Cocivera 1992) for the electrodeposited CdSe films.

4. Conclusion

The results of the present study indicate that successive pulse plating improves PEC characteristics. There is reason to expect that quantum efficiency and power conversion efficiency can be enhanced further by optimizing the heat treatment and etching steps and also pulse parameters.

Acknowledgement

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Influence of deviation from stoichiometry on the photoluminescence in CdTe doped with indium

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Abstract. Low temperature photoluminescence of vacuum and cadmium annealed CdTe:In is reported here. A new peak at ~ 1.14 eV related to transitions from the conduction band to an acceptor involving a tellurium vacancy has been observed.

Keywords. Cadmium telluride; photoluminescence; annealing; stoichiometry; indium doping.

1. Introduction

Cadmium telluride is an important substrate material used in the advanced $\text{Ga}_{1-x}\text{Cd}_x\text{Te}$ (MCT) programme. It is important not only as a substrate for epitaxy, but also as an active part of potential heterojunction device structures, in the fabrication of nuclear detectors, solar cells, etc. All these applications are very sensitive to the purity of samples, particularly, if cadmium telluride is to be used as a substrate for epitaxial growth of MCT, since outdiffusion of the impurities into the epilayer during growth and subsequent annealing will impair the performance of MCT detector. Many recent investigations, designed to identify various types of acceptor impurities, have employed nondestructive techniques such as EPR and low temperature photoluminescence spectroscopy (Molva *et al* 1982).

Although, photoluminescence spectroscopy is a sensitive, nondestructive technique that can provide valuable information concerning the type and distribution of defects and impurities in a crystal, the interpretation of PL data in II-VI semiconductors is not straight forward because of the complex nature of the defects introduced by deviations from stoichiometry and the interaction of these defects with the dopant atoms. Hence, the results obtained by different groups do not necessarily agree and some interpretations are contradictory.

Self-compensation phenomena in halogen doped cadmium telluride has been extensively studied by Bell *et al* (1974). Indium (a donor) is often intentionally introduced into CdTe for the purpose of compensating native defects and producing semi-insulating material. The present understanding of defects in CdTe is rather meagre. Definitive information on the microscopic structure of native defects is lacking.

Most PL studies on CdTe have been restricted to the energy range above ~ 1.24 eV. The commonly observed features in the 4.2 K PL spectra of CdTe are a series of sharp peaks in the range 1.5–1.6 eV attributed to excitonic and near band edge emissions, 1.42 eV band with phonon replicas and a broad band around 1.1 eV. There have been only a few reports on the 1.1 eV and lower energy bands. The 1.1 eV band in bulk CdTe samples as reported by a few groups is thought to be

due to transitions from a deep level formed (de Nobel 1959; Lorentz and Segall 1963; Vavilov *et al* 1967; Das *et al* 1990) as a result of deviation from stoichiometry. But, regarding the 1.42 eV defect peak there has been a lot of controversy, with different groups assigning different transitions to it (Vavilov *et al* 1967; Rud *et al* 1971; Das *et al* 1990; Babentsov *et al* 1992). Despite the prominence of 1.42 eV bands and their long history of observation, the possible origin of this band still remains a matter of dispute and conjecture.

Heat treatments under tellurium or cadmium overpressure are of particular interest because the overall stoichiometry of the crystal can be changed. Suitable conditions for the observation of PL spectra can be achieved, for example, by brief thermal annealing in vapours of the components of the semiconductor. In this paper we report the 4.2 K PL of vacuum and cadmium annealed CdTe doped with indium and the presence of a new peak related to a tellurium vacancy.

2. Experimental

Indium doped CdTe crystals, grown by the asymmetrical Bridgman method (Bagai and Borle 1989) have been used in the present investigation. In this method, the growth ampoule is held asymmetrically inside a cylindrical furnace and crystals are grown by lowering the ampoule vertically through the temperature gradient of about $10^{\circ}\text{C cm}^{-1}$ at a speed of 0.5 mm h^{-1} . Single crystal wafers of CdTe:In oriented along $\langle 111 \rangle$ directions were cut from the grown ingot from which samples of required dimensions were prepared. Typical sample size was $3 \times 5 \text{ mm}^2$. All the cut samples were chemically etched in 1% bromine in methanol for 5 min followed by rinsing for 1 h in methanol to remove traces of bromine. After this, the samples were treated in 1 N KOH in methanol for 5 min to remove the tellurium film resulting in the bromine methanol etch (Amirtharaj and Pollak 1984).

Cadmium annealing was done by placing the CdTe sample in a sealed evacuated dumb bell shaped ampoule in presence of an excess cadmium vapour pressure. The cadmium vapour atmosphere was created by placing a suitable amount of high purity (6 N) cadmium in the ampoule at the same temperature as the CdTe sample. Vacuum annealing was done by placing CdTe sample in a sealed evacuated quartz ampoule without cadmium. Both the annealings were carried out at 650°C for 6 h. Samples were quenched immediately after annealing in liquid nitrogen. A piece of the original sample which was taken from the adjacent part of the wafer and which was not annealed was kept as a control sample (for the sake of comparison).

Photoluminescence measurements were carried out at 4.2 K using MIDAC Fourier Transform PL system. An Argon ion laser operating at a wavelength of $5145 \text{ \AA}$ was used as a source of excitation. The exposed sample area was $\approx 3 \text{ mm}^2$. Neutral density filters were used to record the spectra at high laser powers. PL signal was detected by a LN_2 cooled Ge-photodetector whose operating range is about 0.75–1.9 eV. Measurements were carried out with a resolution of 0.5 meV.

3. Results and discussion

PL measurements were performed on all the pieces cut from a single CdTe:In wafer, prior to annealing treatments. PL spectra recorded were essentially the same

the changes caused by annealing and not to differences in the starting materials. A typical photoluminescence spectrum of CdTe:In is shown in figure 1. The main features as can be seen are the 1.1 eV broad band (attributed to cadmium vacancies), the 1.4 eV peak with phonon replicas (controversial band) and the 1.54 eV edge emission. Figure 2 shows the PL spectra of the 1.11 eV broad band of the control, vacuum and cadmium annealed samples recorded at 4.2 K at a laser excitation power of 100 mW. It is clearly evident from spectra (a) and (b) in this figure that there is a 15 fold increase in the peak height and approximately 8 times increase in the integrated intensity on vacuum annealing. Table 1 gives the integrated intensity for

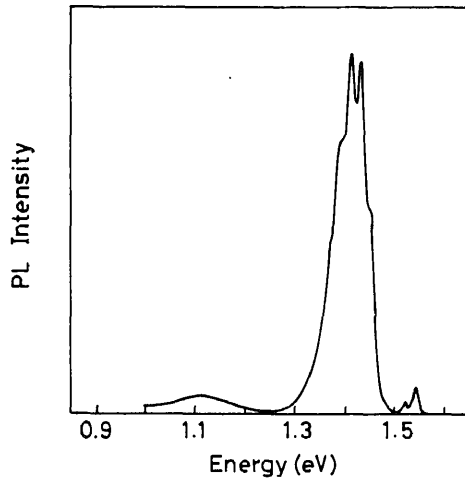


Figure 1. PL spectrum of CdTe:In at 4.2 K in the range 0.9–1.6 eV.

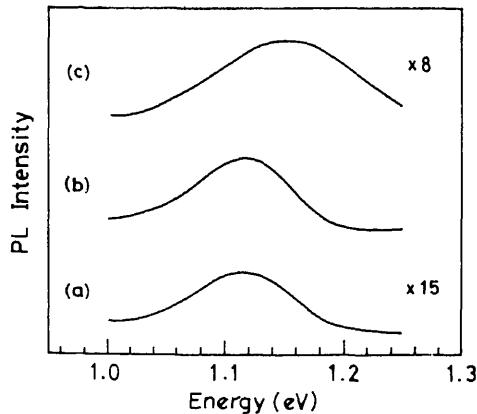


Figure 2. PL spectra at 4.2 K showing the 1.11 eV band in (a) control, (b) vacuum annealed and (c) cadmium annealed CdTe:In samples (Excitation power: 100 mW).

various peaks in the control and annealed samples. However, this peak as seen from spectrum (c) is found to have disappeared in the sample annealed in a cadmium atmosphere. This suggests that the band is related to transitions from a native defect involving a cadmium vacancy. Vavilov *et al* (1967) attributed this band to electron transitions from the doubly charged state of the double acceptor at ($E_c - 0.6$ eV) to the valence band. Sobiesierski *et al* (1988) have shown that the PL bands at around 1.11 eV in chemically etched bulk samples are a result of deviation from stoichiometry. However, the few reports by Kernocker *et al* (1985) and Bowman and Cooper (1988) suggest the band around 1.11 eV to arise from some iron impurity.

Figure 3 shows the PL spectra of 1.4 eV band of the control, vacuum and cadmium annealed samples recorded at 4.2 K at 100 mW laser power. This band which occurs independent of growth technique has not been identified and its origin is therefore widely discussed. This band has the zero phonon line at 1.453 eV. The peak intensity of this band in vacuum annealed sample decreased by approximately 5 times and about 1.5 times in cadmium annealed sample. However, the integrated intensity of this 1.4 eV band in the vacuum annealed sample as can be seen from table 1, decreased by ~ 1.3 times and increased by ~ 1.5 times in the cadmium sample when compared to the control sample. A shift of the peak energy of ~ 4 meV for a decade change in the excitation intensity can be seen from figures 4a

Table 1. Integrated intensity of the PL peaks of the control and annealed samples.

Sample	Laser power (mW)	Integrated intensity (au)		
		1.116 eV	1.146 eV	1.4 eV
Control	100	5	–	21
Vacuum annealed	100	39	–	16
Cadmium annealed	100	–	9	35

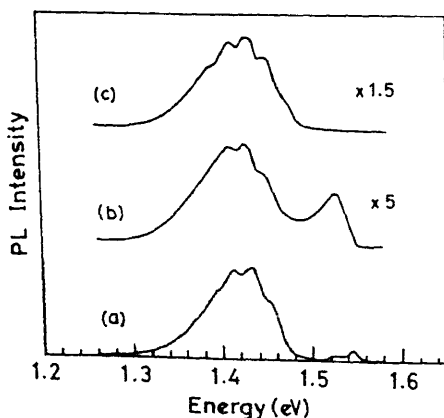


Figure 3. PL spectra at 4.2 K showing the 1.4 eV band in (a) control, (b) vacuum annealed and (c) cadmium annealed samples. (Excitation power: 100 mW).

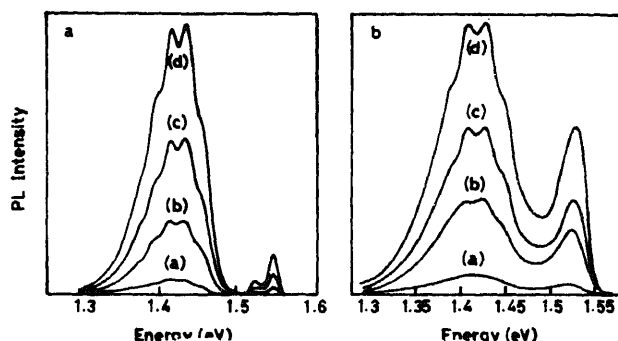


Figure 4. PL spectra at 4.2 K recorded at different excitation intensities of (a) control and (b) vacuum annealed samples. (Excitation intensities: (a) 10 mW, (b) 50 mW, (c) 150 mW and (d) 250 mW).

and b for the control and vacuum annealed samples respectively. This shift suggests this band to involve a D-A transition, which is in agreement with earlier reports (Rud *et al*; 1971, Das *et al* 1990; Babentsov *et al* 1992).

The transition responsible for this band in all CdTe crystals has been interpreted in various ways. According to de Nobel (1959) the band has been attributed to D-A like transitions. D-A transition has been one of the other interpretation by various groups (Rud *et al* 1971; Das *et al* 1990; Babentsov *et al* 1992). There has been a lot of speculation regarding the donors and acceptors involved in the transition. Some groups have assigned this band to transition from shallow donors to deep acceptors involving a cadmium vacancy (Vavilov *et al* 1967), while others to transition from donors formed by interstitial cadmium atoms to acceptors (Vavilov *et al* 1967; Rud *et al* 1971). Our results on the effect of cadmium vapour pressure on the luminescence intensity make it difficult to attribute the 1.4 eV band to cadmium vacancy. D-A complex of the type $\text{Cd}_i\text{-X}$ may possibly be involved in this transition. However, further investigations must be carried out before any conclusion can be drawn. Investigations by Hofmann *et al* (1992) clearly show that the emission in this spectral range consists of (at least) three independent emission bands, the first one located at 1.45 eV involving a D-A transition (Chamonal *et al* 1982), the second one of unknown origin at 1.475 eV (Onodera and Taguchi 1990) and the third one at 1.478 eV (Hofmann *et al* 1992) arising from a D-A recombination involving the A-centres. It should be noted that all these bands have completely different origins and unfortunately interfere in most of the samples leading to considerable discrepancy.

The edge emission at 1.544 eV as seen from figures 3 (spectrum a) and 4a is attributed to a C-A transition as the peak energy does not vary with excitation intensity (Agrinskaya *et al* 1971; Barnes and Zanio 1975). The acceptor involved is a singly ionized cadmium vacancy. The hump seen at 1.523 eV is the LO phonon replica of the 1.544 eV peak. Excitation intensity dependence of the peak energy can be seen in figure 4a.

However, the edge emission at 1.528 eV as seen from figures 3 (spectrum b) and 4b is a D-A transition as the peak energy shifted by ~ 4 meV per decade

change in the excitation intensity (Agrinskaya *et al* 1971). The acceptor is a cadmium vacancy with an ionization energy of 60 meV as reported earlier. It can be seen from spectrum (c) in figure 3 that the edge emissions have disappeared in the cadmium annealed sample.

Spectrum (c) in figure 2 shows a peak at ~ 1.146 eV. A level at $E_v + 0.46$ eV corresponding to a tellurium vacancy has been reported in the literature (Caillot 1972). Halsted *et al* (1961) for CdTe and Uchida (1964) for ZnS and CdS have shown that a cation deficiency results from firing in an over-pressure of the anion and *vice versa*. This shows that firing the sample in an over-pressure of cadmium has resulted in the formation of tellurium vacancies and hence the 1.146 eV peak can be attributed to C-A like transitions involving the tellurium vacancy. To confirm the origin of this peak in our spectrum, the cadmium annealed sample was again subjected to a further annealing at 650°C for 6 h, but in a saturated tellurium atmosphere. Figure 5 shows the PL spectra of the control, cadmium annealed and subsequent tellurium annealed samples. The disappearance of the 1.146 eV peak and reappearance of the 1.116 eV peak after tellurium annealing confirms that the 1.146 eV peak is to be related to transitions involving tellurium vacancy. No shift of this peak with excitation intensity was observed. The decrease in the peak intensity of the 1.4 eV band in the tellurium annealed sample as compared to the cadmium annealed one (figure 6), suggests that the 1.4 eV band does not involve a cadmium vacancy. So, firing of the sample in a tellurium atmosphere has resulted in the formation of cadmium vacancies, which is confirmed by the reappearance of the 1.116 eV band and the decrease in the intensity of the 1.4 eV band.

The edge emission at 1.532 eV as seen from figure 6 (spectrum b) is again a D-A like transition with ~ 10 meV/decade shift in the peak energy. A large shift of this magnitude and more has been seen in compensated GaAs (Yu 1977; Swaminathan *et al* 1981a) and AlGaAs (Mazzaschi *et al* 1980; Swaminathan *et al* 1981b) and in moderately doped InP (Swaminathan *et al* 1985). Such a large shift with excitation can happen either when the material is closely compensated or if

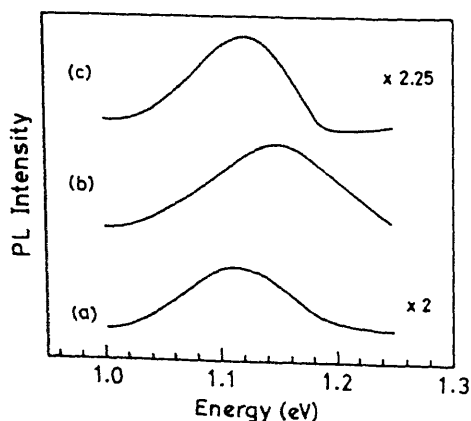


Figure 5. PL spectra at 4.2 K showing the 1.116 eV and 1.146 eV bands in (a) control, (b) cadmium annealed and (c) tellurium annealed subsequent to cadmium annealing samples. (Excitation power: 100 mW).

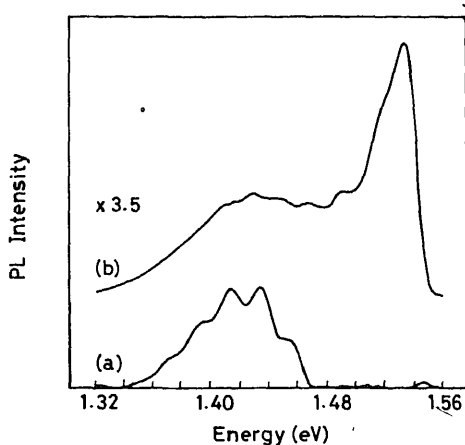


Figure 6. PL spectra at 4.2 K showing the 1.4 eV band and the edge emissions in (a) cadmium annealed and (b) tellurium annealed subsequent to cadmium annealing samples. (Excitation power: 100 mW).

the donor or the acceptor involved is a deep one. More experiments are needed to verify this and work in this direction is under progress.

Conclusions

Our PL results show the 1.116 eV peak in the vacuum annealed sample to involve cadmium vacancy. The annealing experiments in cadmium and tellurium overpressure suggests that the 1.146 eV peak in cadmium annealed sample to involve a tellurium vacancy and 1.4 eV peak to involve transitions from shallow interstitial cadmium donors to acceptors.

Acknowledgement

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Polyetherurethaneurea reinforced poly(vinyl alcohol) dialysis membranes: studies on permeability and mechanical strength

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Abstract. Poly(vinyl alcohol) is a hydrogel which is extensively studied for a variety of biomedical applications. Membranes developed from crosslinked poly(vinyl alcohol) (PVA) is having excellent permeability to solutes. However its wet breaking strength is low. Polyetherurethaneurea (PEUU), having an excellent mechanical strength is blended with PVA as a reinforcement, and membranes developed are studied for its permeability and mechanical strength. The optimum membrane selected, is having permeability and wet breaking strength almost equal to the commercially available cellulose acetate membrane.

Keywords. Haemodialysis membrane; permeability; poly(vinyl alcohol); mechanical strength.

1. Introduction

The vital part of the extracorporeal haemodialyser is the semipermeable membrane that removes certain toxic substances from blood by diffusion. Haemodialysis membranes should have high permeability to solutes, should be blood compatible and should be able to withstand the maximum transmembrane pressure (DHEW 1977). Regenerated cellulosic membranes are currently being used on the largest scale in haemodialysis (Hudson and Cuculo 1980; Ikada 1991) because of its good mechanical strength and solute permeability. Since permeability is directly related to the molecular weight of the solutes, there is little selectivity in the filtering of closely related molecules through cellulosic membranes (Lyman 1964; Hudson and Cuculo 1980), and is known to activate complement system (Ikada 1991). Hence novel membranes need to be developed with good selectivity and mechanical strength.

Poly(vinyl alcohol) (PVA) is used as a basic material for a variety of biomedical applications including contact lens material (Peppas and Yang 1980; Yang *et al* 1981), skin replacement material (Hogemann *et al* 1961; Charadack *et al* 1962), reconstruction of vocal cords (Peppas and Benner 1979, 1980), articular cartilage replacement (Peppas 1979) etc. But its main disadvantage is its weak mechanical strength (Peppas and Merrill 1977). Partial crystallization by annealing can increase the mechanical strength by 100 fold (Peppas and Merrill 1976). Efforts are also being made to use PVA membranes for artificial kidney applications (Merrill *et al* 1972; Peppas 1977; Aleyamma and Sharma 1988), but its commercial application is limited due to lack of adequate wet breaking strength. With proper composition of hydrophilic and hydrophobic regions, membranes with ample strength and

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permeability can be developed. Many studies have been carried out in this direction (Yamashita *et al* 1979; Ohtsuka *et al* 1980).

We have attempted to develop membranes based on PVA having wet-breaking strength comparable with cellulose acetate membrane. Membranes are prepared from crosslinked PVA by blending PEUU as a reinforcement material in various ratios. Its mechanical and permeability properties are studied.

2. Materials and methods

Polyetherurethaneurea (PEUU 1000) was synthesized by solution polymerization in our laboratory as described elsewhere (Shibatani *et al* 1977). Poly(vinyl alcohol), (MW = 125000, 88% mole hydrolized) was from Polysciences Inc. Standard cellulose acetate membrane (0.1 mm thickness) from Thomas Scientific, Swedesboro, USA was used as control. All chemicals used were of AR grade.

2.1 Preparation of membranes

PVA solution (10g% W/V) prepared in dimethyl sulphoxide, and paraformaldehyde was mixed in the ratio 1:1 (w/w) and heated to 60°C. To this 0, 2.8, 4.4 and 6.25 ml of PEUU (20g% W/V) was added and mixed well for 30 min, to obtain blends of different ratios. The solution was kept for sometime to get rid of airbubbles, and spread over a glass plate and heated in an oven at 60°C for 48 h. Membranes were peeled off from glass plate, soaked in con.NaOH solution for 1 h, washed in distilled water and kept overnight in DW. These membranes were of 0.1 mm thickness.

2.2 Octane contact angle

Here the octane/water method was selected as a probe for investigating the polar interactions across polymer/water interface (Hamilton 1972). Contact angle was measured using a goniometer (Kernco Instruments Inc., Texas, USA) as described by Chandy and Sharma (1987). At least 30 angles were measured on each surface, averaged and expressed with standard deviations.

2.3 Degree of hydration

Samples cut in the shape of a disc of equal area were weighed and dipped in DW to attain equilibrium swelling. Samples were taken out of water, blotted with filler paper and the weights determined. The degree of hydration was calculated as

$$QW(\%) = (X_2 - X_1)/X_1 \times 100.$$

where X_1 is the weight of dried samples and X_2 the weight of swollen samples.

2.4 Mechanical strength evaluation

Tensile strength and elongation at break were measured according to the method

of ASTM-D 882 using Universal test machine (Chatillon UTSE-2) at a cross head speed of 2.54 cm/min, at room temperature. For wet strength, dimensions of swollen samples were used for calculation.

2.5 Permeability studies

An equilibrium type dialysis cell (3784-D, Arthur H. Thomas Co. USA) was used for determining the permeability of solutes through the membrane at room temperature.

The membrane was clamped between the two compartments using suitable supporting and sealing device. One compartment was filled with phosphate buffer (pH 7.4) and the other with a mixture of solutes containing urea (100 mg% M.W., 60), creatinine (10 mg%, M.W., 113), uric acid (10 mg%, M.W. 168), inulin (25 mg%, M.W. 5000) and albumin (100 mg%, M.W. 69000) in 0.1 M phosphate buffer, pH 7.4. The permeability of solutes through the membrane for 4 h were analyzed spectrophotometrically employing diacetyl monoxime reagent for urea (Latting 1964), alkaline picric acid for creatinine (Hawk 1965), Folin-Wu method for uric acid (Hawk 1965), phenol-sulphuric acid for inulin (Hodge and Hofreiter 1962) and Folin's reagent for albumin. Permeability percentages were calculated from triplicate experiments.

3. Results and discussion

From the octane contact angle studies (table 1), it seemed that as the concentration of PEUU was increased the membranes became comparatively hydrophobic. Degree of hydration of the membranes also decreased as the PEUU content increased. This may be due to the induced hydrophobic moiety of PEUU which is relatively a hydrophobic polymer. Swelling of hydrogel membranes are mainly due to their amorphous regions (Peppas 1987). Blending makes a decrease in the non-crystalline region which decreases the swelling property of the membranes. Compared to bare PVA membranes the tensile strength of blended membranes (dry and swollen state), increased with the increase in PEUU concentration (table 2). PEUU is a block copolymer containing blocks of low molecular weight polyethers linked together by a urethane group, with an excellent tensile strength and high flexure endurance (Szycher 1991). The wet breaking strength significantly increased when the PEUU content was increased to 20%.

Solute permeability of blended membranes from a mixture of different solutes are given in table 3. Solute permeability is reported as the percentage passed in 4 h as a comparative data. It seems that solute permeability decreased with the PEUU concentration. However it is more than that of cellulose acetate membrane. Even though the blending significantly increased the mechanical properties, the decrease in the degree of hydration had a negative impact on the permeability. It is reported that modifications that increase the strength usually decrease the permeability and methods that improve the permeability degrade the mechanical property (Muir *et al* 1973). Based on the free volume theory of diffusion Yasuda *et al* (1968) indicated that the diffusive permeability of solutes through hydrogel membranes is explained by water content. For PVA films, permeation of water, or water soluble solutes is reported to be dependent on the degree of swelling (Kojima

Table 1. Octane contact angle and degree of hydration of PEUU blended PVA membranes.

Membranes	Percentage of		Octane contact angle (degrees)	Degree of hydration (%)
	PVA	PEUU		
Bare PVA	100	—	135± 4	110
PVA 90/10	90	10	129± 4	105
PVA 85/15	85	15	124± 2	100
PVA 80/20	80	20	118± 3	84
Bare PEUU	—	100	112± 3	11
CA	—	—	130± 3	49

CA, Cellulose acetate.

Table 2. Tensile strength and elongation of PEUU blended PVA membranes.

Membranes	Tensile strength (kg/cm ²)		Elongation (%)	
	Dry	Wet	Dry	Wet
Bare PVA	410± 26	221± 21	255± 16	847± 31
PVA 90/10	431± 26	289± 26	210± 28	794± 16
PVA 85/15	492± 31	305± 23	201± 24	750± 33
PVA 80/20	515± 30	335± 19	194± 33	706± 39
CA	437± 29	394± 11	61± 5	82± 4

Table 3. Permeability of solutes through PEUU blended PVA membranes in 4 h.

Membranes	Permeability (% passed ± S.D.)				
	Urea	Creatinine	Uric acid	Inulin	Albumin
Bare PVA	58.9± 2.2	32.2± 1.5	23.5± 1.1	7.3± 0.5	1.5± 0.5
PVA 90/10	56.0± 2.9	26.4± 1.2	21.6± 2.1	6.3± 0.7	1.4± 0.5
PVA 85/15	53.6± 2.6	26.1± 1.2	20.9± 1.1	5.9± 0.6	1.4± 0.6
PVA 80/20	50.1± 2.0	25.5± 1.0	20.9± 2.1	5.9± 0.7	1.3± 0.5
CA	46.2± 1.9	31.5± 1.5	24.3± 0.5	5.8± 0.2	2.9± 0.6

et al 1983). Here also it seems that permeability may be directly proportional to the equilibrium water content.

The membrane with 80/20 blend ratio is selected compromising the mechanical strength and permeability. Further increase in PEUU content, may increase the wet breaking strength, but it will decrease the permeability.

Membranes used for haemodialysis should be highly blood compatible. It is known that cell adhesion is greater on hydrophilic substrates compared to hydrophobic one (Baier 1977), and the adhesion of platelets onto the material surface initiates the thrombus formation (Szycher 1983). Since the blended membranes are comparatively more hydrophobic, cell adhesion onto these surfaces may be less than that of PVA. PVA and PEUU is reported to be highly blood compatible (Ikada *et al* 1981; Szycher 1991). Low clotting tendency of polyurethanes (Boretos

and Pierce 1968) makes them useful in biomedical devices like vascular graft, heart valve, artificial kidney membranes, artificial heart and assist devices (Boretos *et al* 1971; Lyman *et al* 1977). Blood compatible membranes are also being developed (Jayasree and Sharma 1989) from PEUU. However, further studies are required to evaluate the blood compatibility of the blended membranes.

4. Conclusion

From this study it has been shown that the mechanical properties and dialysis performance of PVA membranes are varied by adjusting the blending ratio of PVA and PEUU. Membrane with 80/20 blend ratio is having the highest tensile strength with comparable permeability to cellulose acetate. This membrane showed the possibility of having appropriate mechanical strength and solute permeability suitable for the possible application as dialysis membrane.

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Gas permeabilities of bisphenol bridge-disubstituted polyarylates

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Abstract. This study reports the physical properties and gas permeation characteristics of polyarylates prepared by disubstitution of the bisphenolA bridge carbon. The results are compared with data from previously reported unsubstituted and mono-substituted polyarylates. Disubstitution is an effective method of changing the packing density, as measured by the d-spacing, and also increases the chain stiffness. The intersegmental spacing can be either decreased (by phenyl disubstitution) or significantly increased (by $-\text{CF}_3$ disubstitution). Increased d-spacing in the case of $-\text{CF}_3$ disubstitution increases permeabilities and reduces selectivities compared to the unmodified bisphenolA based polymer. The increased permeability and selectivity of the phenyl disubstituted polyarylates, in spite of the reduced d-spacing, supports an earlier finding that decreased bisphenol phenyl ring mobility tends to increase permeability.

Keywords. Permeability; polyarylates; gas separation.

1. Introduction

The economic viability of a membrane gas-separation process depends greatly on the permeation characteristics of the membrane material. The ideal membrane material would have high permeability (P) coupled with high permselectivity (α) for the gas pair under consideration. Unfortunately, the trend observed with most materials shows a trade off, i.e. membrane materials which have high permeability have low selectivity and *vice versa*. A better understanding of the polymer structure-permeability relationship is required for synthesizing polymers with the desired permeation characteristics.

In order to take advantage of the naturally higher selectivities in glassy polymers, recent work has focussed on polymers such as polyimides (Kim *et al* 1988; Stern *et al* 1988; Coleman and Koros 1990), polycarbonates (Anand *et al* 1989; Schmidhauser and Longley 1990), polysulfones (McHattie *et al* 1991; Houde *et al* 1994a) and polyarylates (Sheu and Chern 1989; Charati *et al* 1991a). Polyarylates based on bisphenolA have been identified as having potentially higher permeabilities than other glassy polymers (Barbari *et al* 1989).

The structure of polyarylates can be modified by varying either the diol or acid monomers. For rational design, it is necessary to identify the effect of various structural modifications on the permeation characteristics.

In this context, recently, we prepared a series of polyarylates in which one methyl group on the bisphenol bridge carbon was systematically substituted by other groups, e.g. ethyl, isobutyl, phenyl and ethyl propionate (Houde *et al* 1994b).

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Testing of the polymers resulting from these monosubstituted bisphenols and a 1:1 mixture of iso and terephthalic acids showed two unusual results: (i) the packing density of these polymers as measured by their d-spacing (obtained from wide angle X-ray diffraction) or free volume (obtained from density measurements) did not vary significantly even though the methyl group was substituted by much bulkier groups and (ii) there was significant (3-fold) variation in the permeabilities of the various monosubstituted polymers. Surprisingly, increased permeability correlated well with decreased rotational mobility of the bisphenol phenyl rings (measured by the γ -transition in dynamic mechanical analysis). This result is contrary to theories (e.g. Pace and Daytner 1979) of gas permeation as well as previous interpretations (Light and Seymour 1982) of the permeability data in partially aliphatic polyarylates.

The present study is an attempt to build our understanding of the factors affecting permeation in substituted polyarylates. Molecular modelling (CharmM Quanta 2.1) indicates that these bridge carbon substituents are oriented towards the outside of the polymer chain helix. This is illustrated in figure 1 which shows minimized single chain conformation of a polyarylate prepared from isobutyl substituted bisphenolA (bisMIBK) and terephthalic acid in comparison with the unsubstituted polymer. The chain conformation in the vicinity of the bisphenol moiety is determined by the phenyl ring orientations. These orientations, in an energy minimized conformation, are determined by the repulsive interactions between the ortho hydrogens on the phenyl rings and the influence of the substituents on the bridge carbon (Charati *et al* 1991b). Based on the molecular modelling work, we hypothesized that if the bridge carbon was disubstituted, it would not be possible for the chain configuration to remain unaffected. If this was true, disubstitution might be an effective way of changing the polymer packing density, and thereby the permeation characteristics. Secondly, the disubstitution of the bridge carbon by rigid groups should lead to reduced segmental mobility and would be an additional data regarding the effect of this variable on permeability.

In this study, we describe the permeation characteristics of polyarylates based on two disubstituted bisphenols and iso- and terephthalic acids. The bisphenols used were: (i) phenyl disubstitution (bisBzp) and (ii) $-\text{CF}_3$ disubstituted (bisF₆). The results are compared with the corresponding polymers based on bisphenolA and the mono-phenyl substituted bisphenol (bisAceto). The chemical structures and nomenclature of the polymers discussed here are shown in figure 2.

2. Experimental

2.1 Material preparation

BisBzP was prepared by following the general procedure outlined by Morgan (1970). In the first step, dichlorodiphenylmethane (DCDPM) was prepared by Friedel-Craft alkylation of CCl_4 with benzene. To a stirred suspension of AlCl_3 (10 g, 0.075 mol) in 25 ml of CCl_4 , 11.7 g of benzene (0.15 mol) were added dropwise for 1 h, maintaining the temperature at 5°C. After the addition, the temperature of the reaction mixture was raised to ambient and left overnight. 25 ml of CH_2Cl_2 were added to dilute the reaction mixture, which was then poured on crushed ice

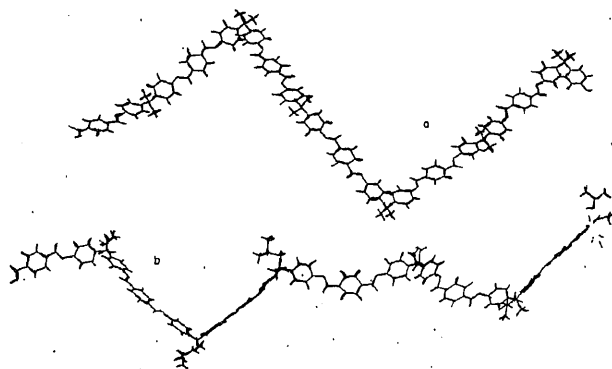
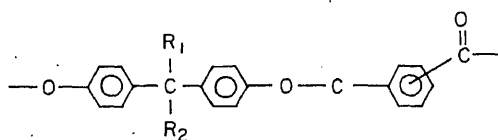


Figure 1. Representation of energy minimized single chain conformation for polyarylates based on terephthalic acid and (a) bisphenol A and (b) bisphenol A with isobutyl substitution, showing orientation of the bridge carbon substitution.



<u>POLYMER</u>	<u>R₁</u>	<u>R₂</u>	<u>ACID</u>
Bis A - I	-H	-H	Iso
Bis A - T	-H	-H	Tere
Bis A - I + T	-H	-H	Iso + Tere (1:1)
Bis Aceto - I + T	-H		Iso + Tere (1:1)
Bis Bzp - I + T			Iso + Tere (1:1)
Bis Bzp - I			Iso
Bis F ₆ - I + T	-CF ₃	-CF ₃	Iso + Tere (1:1)

Figure 2. Chemical structure of polyarylates.

containing a few drops of concentrated HCl. On stirring to break the AlCl₃ complex, the organic layer separated and the aqueous layer was extracted twice with CH₂Cl₂. The combined organic layer was dried over Na₂SO₄ for about 3 h and the solvent was removed by distillation. Traces of the solvent were removed at low pressure. Thin layer chromatography of the resulting brown, viscous liquid showed only a trace amount of benzophenone impurity in the DCDPM.

In the second step, two molar equivalents of phenol were added to DCDPM. The reaction mixture was stirred overnight at 60°C and then heated at 170°C for

around 5 h till it solidified. The bisphenol was dissolved in NaOH solution and reprecipitated by dilute HCl at 5°C. This was further purified by recrystallization using tetrahydrofuran: cyclohexane. The yield of the pale yellow, shiny needles was found to be 60%. The characterization was done by IR and ^1H -NMR. (i) IR (nujol): 3600–3140 cm^{-1} , broad, -OH stretch, 700 cm^{-1} , O-H out of plane deformation, 1620, 1600, 1520, 1470, 1450 cm^{-1} , aromatic C=C stretch, 1220–1000 cm^{-1} , *m*, C-H (aromatic) in plane bending and (ii) NMR; δ 3–3.1, *s*, hydroxyl protons, D_2O exchangeable, δ 6.75–6.85, *m*, 4H, aromatic, δ 6.95–7.1, *m*, 4H, aromatic, δ 7.15–7.4, *m*, 10H, aromatic.

BisphenolF₆ [4,4'-(hexafluoroisopropylidene)diphenol], isophthalic acid and terephthalic acids were obtained from Aldrich Chemicals (USA) and used without further purification. Isophthaloyl dichloride (IPC) and terephthaloyl dichloride (TPC) were prepared by refluxing their respective acids in thionyl chloride using dimethyl formamide as a catalyst (0.013 molar equivalent for IPC and 0.08 for TPC). Both of them have almost quantitative yield and were characterized by melting point and IR.

2.2 Polymer preparation and characterization

Polymers were prepared by interfacial condensation using either IPC, TPC or their equimolar mixture. Polymers were purified by dissolving in chloroform and reprecipitating in acetone. The purified materials used for forming the polymer films were characterized by the following:

- (i) Glass transition temperatures were determined on a Perkin-Elmer differential scanning calorimeter (model DSC-2C or DSC-7). The heating rate used was 20°C/min.
- (ii) The mean intersegmental spacing (*d*-spacing) was obtained as the length corresponding to the maximum of the amorphous diffraction pattern. Wide angle X-ray diffraction (WAXD) spectra were obtained on a Phillips PW 1730 X-ray generator unit in reflection geometry with Cu-K α radiation. The polymer samples were all amorphous with the exception of bisA-I.
- (iii) Density measurements were done by the flotation method at 40°C using aqueous K_2CO_3 solution.

2.3 Film preparation and permeation study

Films of even thickness ($\sim 50\mu$) were prepared by solution casting from 5% chloroform solutions of the respective polymers. These films were vacuum dried at 65°C for at least eight days and then used for permeation studies. Permeabilities of the pure gases He, Ar, N_2 , O_2 , CH_4 and CO_2 were measured using the variable volume method. The measurements were done at a high side gas pressure of $1 \times 10^6 \text{ N/m}^2$ and 35°C.

3. Results and discussion

The effects of disubstitution at the bisphenol bridge carbon are shown in table 1 which summarizes the data for polyarylates prepared from 4 bisphenols viz, bisA,

bisAceto, bisBzp and bisF₆ with a 1:1 mixture of iso and terephthalic acids. It was previously mentioned that packing density does not change with monosubstitution at the bridge carbon as illustrated by the data for bisAceto-I+T in comparison with bisA-I+T (Houde *et al* 1994b). In contrast, both the disubstituted polymers viz. bisBzp-I+T and bisF₆-I+T show marked changes in packing density as measured by the d-spacing. In the case of the bisBzp based polymer, the decrease in d-spacing to 4.7 Å may be attributed to increased interchain attraction. Such behaviour has been seen before with polar substitutions (e.g. Muruganandam *et al* 1987). In the case of the bisF₆ polymer, the effect is reversed and increased interchain repulsion appears to be responsible for a significant increase in d-spacing to 6.51 Å.

It is generally accepted that the packing density is one of the most important variables affecting the permeability (Stern *et al* 1989; Charati *et al* 1991a). It has been shown that the d-spacing obtained from WAXD data is generally a sensitive and accurate determinant of the permeability of the polymer (Charati *et al* 1991a). In this context, the 3-4 fold increase in permeability for bisF₆-I+T compared to bisA-I+T is in accordance with the increased d-spacing in the case of bisF₆-I+T. The decreased selectivity is also a consequence of the increased d-spacing which reduces the ability of the polymer matrix to discriminate between various gas molecules on the basis of size.

In the same context, it is interesting to compare the data for bisBzp-I+T with bisA-I+T and bisAceto-I+T. Both bisBzp-I+T and bisAceto-I+T have very similar permeabilities and selectivities. In both cases the permeabilities and selectivities are 30-50% higher than for bisA-I+T. This increase can be attributed to the decreased rotational mobility of the bisphenol phenyl rings. This correlation was shown earlier in the case of mono-substituted polymers where the d-spacing did not change markedly within the series (Houde *et al* 1994b). The correlation is even

Table 1. Permeation data and physical parameters of various polyarylates^a.

Property	BisA-I+T	BisAceto-I+T	BisBzp-I+T	BisBzp-I	BisF ₆ -I+T
d-Spacing	5.15	5.09	4.72	4.76	6.51
Density	1.212	1.211	1.217	1.221	1.412
Tg	198	229	251	229	233 ^d
P(He) ^b	16	16	18	16	51
P(Ar)	0.56	0.74	0.79	0.48	2.6
P(N ₂)	0.33	0.32	0.33	0.23	1.5
P(O ₂)	1.4	2.1	1.7	1.3	5.6
P(CH ₄)	0.4	0.48	0.31	0.18	1.35
P(CO ₂)	7.3	11	11	8.4	35
α(Hc/N ₂) ^c	48.5	49.7	53.3	69.6	34.3
α(O ₂ /N ₂)	4.2	6.6	5.3	5.5	3.8
α(CO ₂ /CH ₄)	18.3	22.5	35.2	46.7	25.8
α(N ₂ /CH ₄)	0.83	0.67	1.06	1.28	1.10

^aPolymer nomenclature as given in figure 2; ^bPermeability in units of 10⁻¹⁰ [cm³(STP) cm/cm².sec.cm Hg] measured at 35°C and 1 × 10⁶ N/m²; ^cSelectivity is the ratio of pure gas permeabilities;

^dMaruyama *et al* (1986).

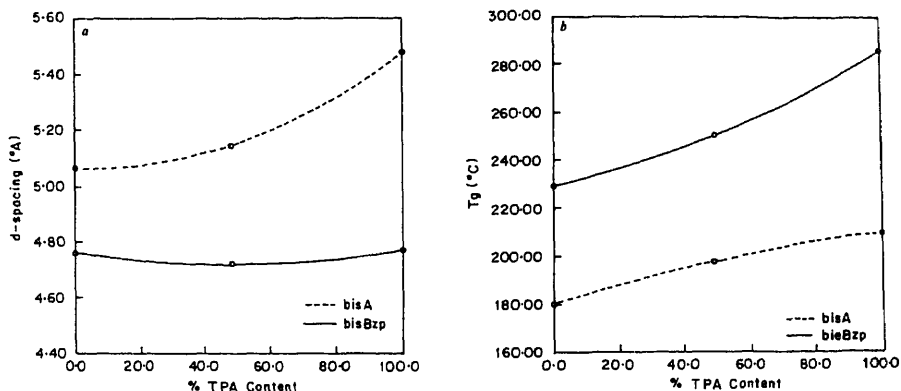


Figure 3. Variation of (a) d-spacing and (b) T_g as a function of terephthalic acid content for polyarylates synthesized from iso- and terephthalic acid and bisA or bisBzp.

stronger in the case of bisBzp-I+T where, in spite of the reduced d-spacing, the increased chain stiffness still leads to higher permeability.

Table 1 shows the data for polyarylates prepared from bisBzp with isophthalic acid in addition to the 1:1 mixture of both iso and terephthalic acids. A common trend in polyarylates is that d-spacing, T_g and permeabilities increase with increasing terephthalic acid content (Vetrivel *et al* 1991; Pessan and Koros 1993). Similar trends have been seen in isomeric analogues for polysulfones (Aitken *et al* 1990) and polyimides (Kim *et al* 1988; Coleman and Koros 1990). However the bisBzp based polyarylates are an exception to this empirical rule. The T_g is increased; however, the d-spacing is constant and consequently the permeabilities are less affected by increasing terephthalic acid content in the bisBzp based polymers. It was not possible to measure permeabilities for bisBzp-T since this polymer is not soluble in common solvents. The difference in the d-spacing and T_g variation with increasing terephthalic content in the bisBzp based polyarylates compared to bisA based polyarylates are shown in figure 3. Molecular modelling suggests that a change in chain colinearity, induced by the modified bisphenol, is responsible for erasing the well-known effect of the acid isomers on chain configuration and packing density.

4. Conclusions

While a previous study (Houde *et al* 1994b) showed that mono-substitution of the bisphenol bridge carbon did not significantly affect the polyarylate packing density, this study shows that disubstitution of this carbon is an effective way of changing the packing density (as measured by the d-spacing) of polyarylates. The d-spacing can be either decreased (by phenyl disubstitution) or significantly increased (by $-\text{CF}_3$ disubstitution). As expected, the disubstitution also increases chain stiffness. Studies with bisBzp based polyarylates prepared with varying acid isomer ratios suggest that the bulky disubstituted groups alter the chain configuration. The variation in d-spacing, commonly seen with varying iso- and terephthalic acid ratios, is absent in these polyarylates.

As expected from the increased d-spacing, bisF₆-I+T has markedly increased permeabilities and reduced selectivities compared to the unmodified bisA based polymer. The increased permeability and selectivity of the bisBzp based polyarylates, in spite of the reduced d-spacing, is in support of the earlier finding (Houde *et al* 1994b) that decreased bisphenol phenyl ring mobility tends to increase the permeability.

Acknowledgements

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Crystallization of polyphenylene sulfide

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Abstract. The properties of molded PPS parts are dependent on the crystalline morphology developed during processing. Even though processed under identical conditions, the crystalline morphology may differ owing to the differences in the crystallization process. The crystallization behaviour of a polymer is known to depend on its molecular architecture which in turn depends upon polymerization process. Thus the study of the crystallization behaviour of polymer with reference to its molecular architecture is essential for obtaining product with desirable properties. In the present paper, the crystallization behaviour of two grades of polyphenylene sulfide was investigated using differential scanning calorimetry (DSC). An attempt has been made to explain the differences in the crystallization behaviour of PPS samples on the basis of the differences in their molecular architecture. The structural differences of PPS manifest themselves in terms of the depression in the equilibrium melting point, retardation of nucleation and overall crystallization rate and coarsening of spherulitic texture.

Keywords. Polyphenylene sulfide; crystallization; curing; morphology.

1. Introduction

Polyphenylene sulfide (PPS) is a high performance engineering plastic with excellent thermomechanical properties, good processability, dimensional stability and chemical resistance (Hill and Brady 1988). Although it exhibits good insulating properties, it can also be made conducting upon doping (Elsenbaumer and Schacklette 1982; Frommer *et al* 1983). It is mainly used in high performance composites, which are used in diverse applications such as aerospace, nuclear plants, radiation equipment, particle physics generators and medical equipment (O'Donnel 1989).

PPS can be synthesized by two methods of polymerization viz. Macallum and Lenz polymerization (Lenz and Handlovits 1960). Macallum polymerization is a heterogeneous reaction of one or more polyhaloaromatic compounds with sulfur and sodium carbonate. The product obtained by this method is mainly branched or lightly crosslinked, whereas Lenz method consists of condensation polymerization of alkali metal salts of *p*-halothiophenols giving a linear structure of PPS. The polymer which is obtained by any of the above two methods is generally a low molecular weight polymer and its molecular weight can be increased by solid state polymerization (Dix 1985). A high molecular weight polymer suitable for injection molding can also be obtained without the solid state polymerization step (Hill Jr 1979). Thus the differences in the synthesis processes can lead to differences in the molecular architecture of PPS.

The properties of molded PPS parts are dependent on the crystalline morphology (Brady 1976; Kohlepp and Kunst 1989). The morphology developed during processing is governed by the crystallization process. It has been well documented that the

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crystallization behaviour is dependent on the processing conditions and inherent crystallization behaviour of the polymer. The crystallization behaviour of a polymer is known to depend on its molecular architecture defined in terms of linearity, molecular weight distribution (MWD), degree of branching etc. Since chemical structure parameters are influenced by the polymerization process, it would be interesting to monitor the changes in the crystallization behaviour of PPS manufactured by two different companies in order to elucidate the differences in their structure. There have been few reports on the effect of structure on the crystallization process of PPS (Jog and Nadkarni 1985; Lovinger *et al* 1985; Lopez and Wilkes 1985; Lopez *et al* 1989; Budgell and Day 1991; Cebe 1992; Neelima Bulakh *et al* 1993a). However, a comparative study of the crystallization behaviour is seldom reported.

The present work attempts to explain the observed differences in the isothermal crystallization behaviour of PPS polymers obtained from different sources on the basis of the differences in their molecular architecture.

2. Experimental

Poly (phenylene sulfide) (PPS), grades Ryton, V-I supplied by Phillips Petroleum (Singapore) (PPS 1) and Fortron, W203 supplied by Hoechst Celanese (USA) (PPS 2) were used for the investigation. The samples were analyzed for their thermal and crystallization behaviour by differential scanning calorimetry (DSC) and also by other analytical techniques such as thermogravimetric analysis (TGA) and optical microscopy (OM).

2.1 Differential scanning calorimetry (DSC)

The non-isothermal and isothermal crystallization studies were carried out using Perkin Elmer DSC 2 equipped with thermal analysis data station (TADS). The melting and crystallization parameters were determined by recording DSC scans at a heating and cooling rate of 10°C/min in nitrogen atmosphere respectively. The temperature and energy scales were calibrated using standard procedures. The melting and crystallization parameters, such as melting point (T_m), heat of fusion, (ΔH_f), temperature of crystallization (T_c) and heat of crystallization (ΔH_c) were used for comparing the two grades.

For non-isothermal crystallization, the samples were heated to 310°C and then cooled at different cooling rates ranging from 2.5 to 40°C/min. The exothermic peaks recorded were then analyzed as per the procedure described earlier (Neelima Bulakh *et al* 1993b).

For isothermal crystallization the sample was heated to melt at temperature 20°C above the melting point for destroying the residual nuclei. It was held at that temperature for a dwell time of 2 min. The sample was then quenched at a rate of 160°C/min to a predetermined crystallization temperature, T_c , at which the crystallization exotherm was recorded on a time base. The exothermic crystallization peak was then analyzed to determine the total crystallization time (t_c) and induction time t_i . The crystallization data were further analyzed and the crystallization parameters were calculated using Avrami theory (Avrami 1939, 1940, 1941).

2.2 Optical microscopy (OM)

The samples were prepared by melt pressing PPS powders between a glass microscope slide and a cover slip and maintained at this temperature to ensure uniform melting. The samples were then transferred to the hot stage and crystallized isothermally at the same temperatures for both the PPS samples. The photomicrographs were then taken using Leica wild MPS 52 with automatic exposure unit on a Leica polarized light microscope.

2.3 Thermogravimetric analysis

Thermogravimetric analysis was carried out using Netzsch-409 thermal analyzer at a heating rate of 10°C/min in nitrogen.

2.4 Curing studies

The samples were kept in preheated air circulatory oven at 385°C and were taken out after 5, 15 and 45 min. The samples were then allowed to cool to room temperature. The cured samples were then analyzed using DSC.

3. Results and discussion

3.1 Melting and crystallization behaviour

The DSC heating and cooling scans for PPS 1 and PPS 2 are shown in figures 1a and b, respectively. Since the as received polymers are used, the melting behaviour exhibit the crystallinity and the morphology of PPS which is developed as a result of the crystallization process during polymerization. It is observed from figure 1a that the two samples exhibit distinct melting peak temperatures at 284°C and 293°C for PPS 1 and PPS 2 respectively. The higher value of the melting peak temperature for the sample PPS 2 relative to PPS 1 indicates higher stability and perfection of the crystallite (Wunderlich 1980). The values of the heat of fusion are 49.1 and 55.4 kJ/kg for PPS 1 and PPS 2 respectively indicating different extent of crystallization for the two samples. This difference may be attributed to the extent of crystallization during polymerization.

The crystallization during cooling takes place at a higher temperature for PPS 2 (253°C) relative to that for PPS 1 (246°C). This might be due to the higher melting peak temperature of PPS 2 relative to that of PPS 1.

The melting behaviour of the melt-crystallized samples (samples crystallized during cooling at a rate of 10°C/min) was studied using the reheating scans. When the melting parameters are compared, it was observed that PPS 1 exhibits a melting peak temperature of 283°C and heat of fusion of 38.2 kJ/kg as compared to 286°C and 45.8 kJ/kg for PPS 2. Thus, even when crystallized under identical conditions, the two PPS samples exhibited different melting peak temperatures and extent of crystallization.

Since the two polymers exhibited distinct melting peak temperatures (even for

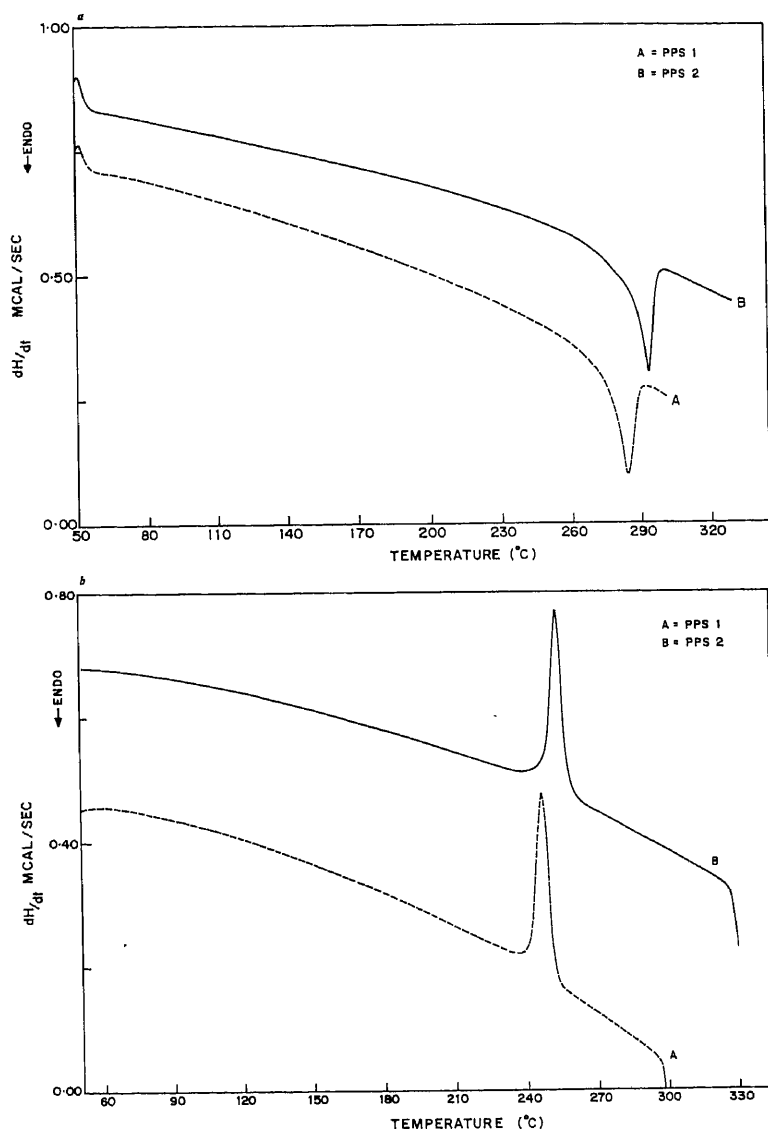


Figure 1. a. DSC heating scans for PPS 1 and PPS 2 samples and b. DSC cooling scans for PPS 1 and PPS 2 samples.

the melt crystallized samples), the equilibrium melting points of PPS samples were determined using the method suggested by Hoffmann and Weeks (1962). The method consists of melting peak temperature measurement of isothermally crystallized polymer samples at selected supercoolings. The experimental melting points are then plotted as a function of crystallization temperature. Figure 2 shows the T_c vs T_m plots for PPS 1 and PPS 2. A straight line relationship between melting and crystallization temperatures is observed. This line is extrapolated to $T_c = T_m$, and

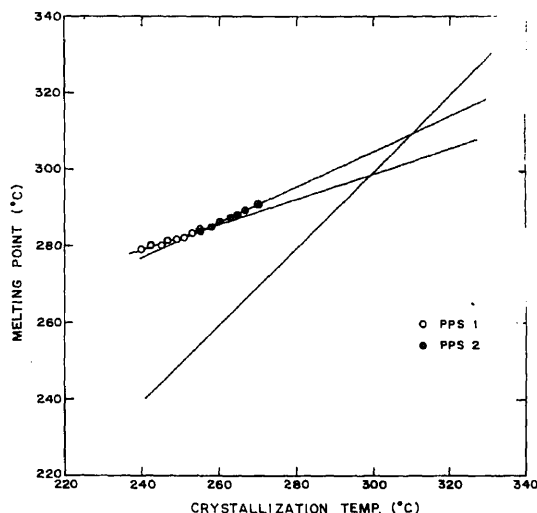


Figure 2. Hoffmann-Weeks plots for PPS 1 and PPS 2 samples.

The point of intersection represents the thermodynamic melting point (T_m°). The calculated values of T_m° for PPS 1 and PPS 2 were 298°C and 308°C respectively. The value of T_m° for PPS 1 was lower than the value of 303°C reported for low molecular weight Ryton V-I (Lovinger *et al* 1985). However, for PPS 2 it was found to be comparable to the value reported for high molecular weight PPS (Lopez and Wilkes 1988). It has been reported that branching decreases the perfection of the crystals resulting in lowering of equilibrium melting point of the polymers. In the case of LLDPE, a monotonic decrease in the melting point with increase in branch concentration has been reported by Mandelkern and Maxfield (1979). Similar drop in equilibrium melting point has also been noted by Lopez *et al* (1989) for linear and branched PPS. The lower value of T_m° for PPS 1 can thus be attributed to lower perfection of the crystals due to the presence of branching.

The non-isothermal crystallization behaviour of the two PPS samples was studied by crystallizing the samples during cooling at different cooling rates. As reported in our earlier publication, the information regarding the crystallizability can be derived from the non-isothermal crystallization data (Neelima Bulakh *et al* 1993b). Figure 3 illustrates the variation of the degree of supercooling ($T_m^\circ - T_c$ onset) with cooling rate. It can be seen that the data can be fitted to a straight line equation. The values of the intercept for PPS 1 and PPS 2 were found to be 19°C and 13°C respectively. The higher value of intercept for PPS 1 suggests that the polymer is less crystallizable as compared to PPS 2. This may be either due to different molecular weights and/or differences in the chemical structure (presence of branching). Since both these factors would influence the crystallization process, the isothermal crystallization behaviour of the two grades of PPS was investigated.

The isothermal crystallization study was carried out over a temperature range of 40°–260°C for PPS 1, and 255°–270°C for PPS 2. The experimental data were analyzed using Avrami's theory (Avrami 1939, 1940, 1941). The induction time, t_0 , and the crystallization half time, $t_{0.5}$ have been chosen as characteristic parameters

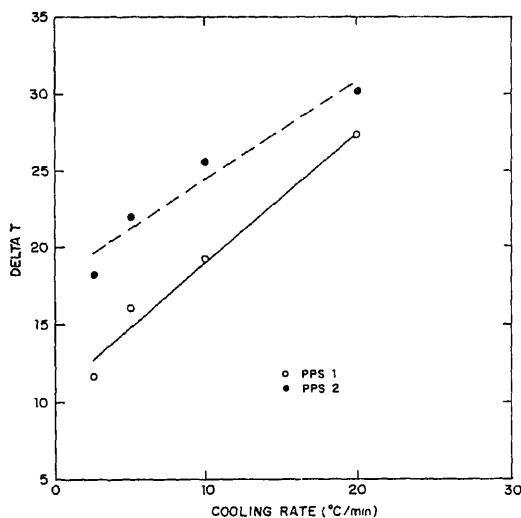


Figure 3. Variation of ΔT with cooling rate for PPS 1 and PPS 2.

for the crystallization process which represent the onset of nucleation and the overall crystallization rate respectively. Since both the polymer samples exhibited different melting points that are about 10° apart, the crystallization parameters are compared as a function of the degree of supercooling instead of the temperature of crystallization. The variation of induction time and crystallization half time with the degree of supercooling (ΔT) is shown in figures 4 and 5 respectively. It is observed that the induction time is lower for PPS 2 over the entire range of supercoolings. Since the induction time represents the characteristic of the nucleation process, the lower values of induction time for PPS 2 suggest that the nucleation of PPS 2 is faster as compared to PPS 1. The variation of the crystallization half time with temperature of crystallization also exhibited similar behaviour indicating that the crystallization rate of PPS 2 is faster than that for PPS 1.

It is well documented that the overall crystallization rate of a polymer decreases with increasing molecular weight. In case of PPS, the overall rate of bulk crystallization was reported to decrease by a factor of ~ 4 over the molecular weight (M_w) range of 24000 to 63000 (Lopez and Wilkes 1988) whereas for branched PPS it was 50% lower than that of linear PPS at comparable molecular weight of about 65000 (Lopez *et al* 1989). In the present study, the observed difference in the crystallization rate thus may be due to the differences in the molecular weight and/or presence of branching. When the crystallization rate values are compared at equal degrees of supercooling it was observed that the crystallization rate for PPS 1 was an order of magnitude lower than that for PPS 2 (figure 6). This clearly suggests that PPS 2 sample has a more linear structure as compared to PPS 1. This contention is also supported by the observed higher value of T_m° for PPS 2 relative to that for PPS 1.

PPS is known to undergo chemical reactions when exposed to high temperatures for prolonged times (Hawkins 1976). Three types of reactions, viz. chain extension, branching and crosslinking are reported. When exposed to temperatures above its

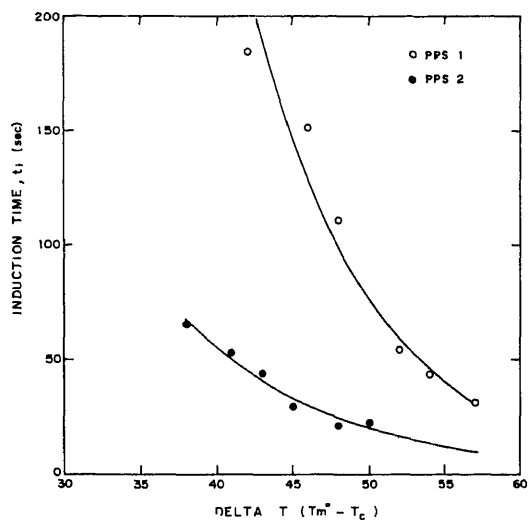


Figure 4. Variation of induction time, t_i with degree of supercooling for PPS 1 and PPS 2 samples.

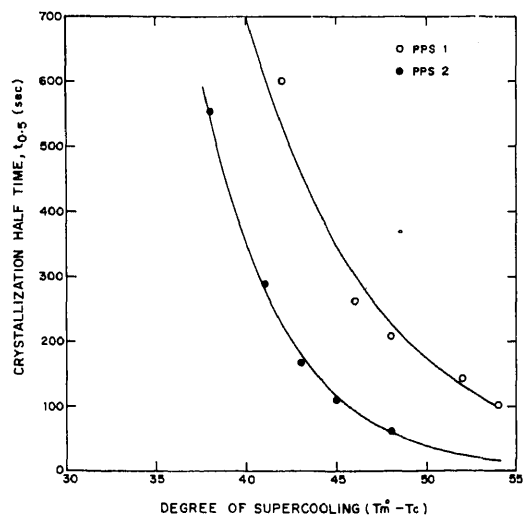


Figure 5. Variation of crystallization half time, $t_{0.5}$ with degree of supercooling (ΔT) for PPS 1 and PPS 2 samples.

melting point in air, crosslinking of PPS takes place leading to decreased crystallizability and crystallinity (Neelima Bulakh *et al* 1993a). The rates of change of degree of crystallinity and crystallizability were found to be dependent on the time, temperature and atmosphere. The response of the two PPS grades to the high temperature exposure was studied to elucidate the subtle differences in their chemical structure. The samples of PPS were cured at 385°C in air for dwell times ranging

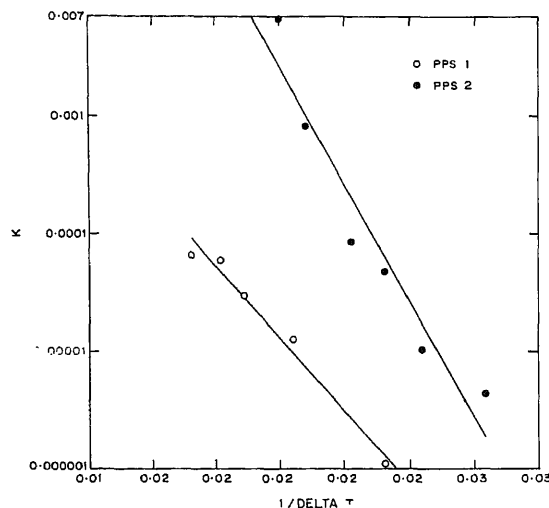


Figure 6. Variation of rate constant K with $1/\Delta T$.

from 5 to 45 min. The effect of the thermal treatment on the heat of fusion is illustrated in figure 7. It is observed that the heat of fusion which represents the degree of crystallinity of the cured sample decreases more rapidly for PPS 2 sample as compared to PPS 1 sample. The curing or crosslinking of PPS is reported to result in a decrease in the crystallinity and crystallizability (Brady 1976). The decrease in the crystallinity of PPS samples with increase in the dwell time thus represents increased degree of curing. Thus the observed results suggest that the degree of curing for PPS 2 sample is higher relative to that for PPS 1 at any given time indicating better thermal stability of PPS 1. In other words PPS 1 undergoes chemical reactions to lesser extent than PPS 2 at high temperature. Black *et al* (1967) have compared the thermal stability of linear and branched PPS samples. They have reported that in general, the thermal stability of PPS samples was dependent on the linearity of the polymer: the higher the degree of branching, the more stable the polymer. Thus the results of curing suggest that PPS 1 is having a more branched structure polymer as compared to PPS 2.

The thermogravimetric analysis in nitrogen atmosphere also exhibited a two-stage degradation process for PPS 1 whereas for PPS 2 it was found to be a single degradation process as illustrated in figure 8. The presence of two distinct steps in the TGA is suggestive of two mechanisms of degradation which may be corresponding to the linear and branched chain structure in PPS 1.

The spherulitic morphology of the two PPS samples was observed using polarized light optical microscope. The micrographs for samples of PPS 1 and PPS 2 crystallized at 235°C are shown in figure 9 at equal magnification using cross polars. It can be seen that both the samples exhibited well defined spherulitic structures. It is also clear from the micrographs that the spherulites differed in size. The spherulite size is larger for PPS 1 than that for PPS 2. It was already observed that the nucleation process for PPS 1 was slower as compared to that for PPS 2. Since the nucleation is slower, the number of nuclei growing at a

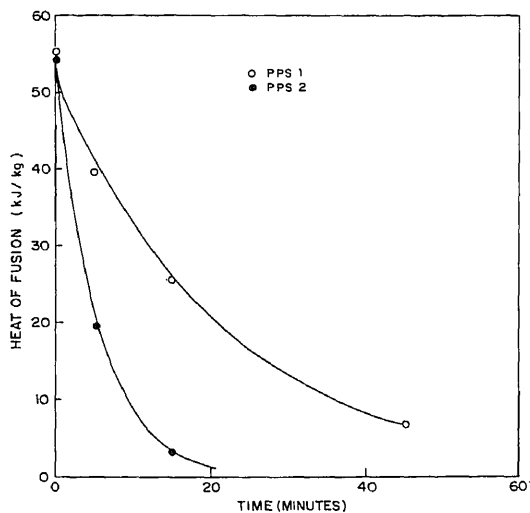


Figure 7. Variation of heat of fusion with dwell time for PPS samples cured in air at 385°C.

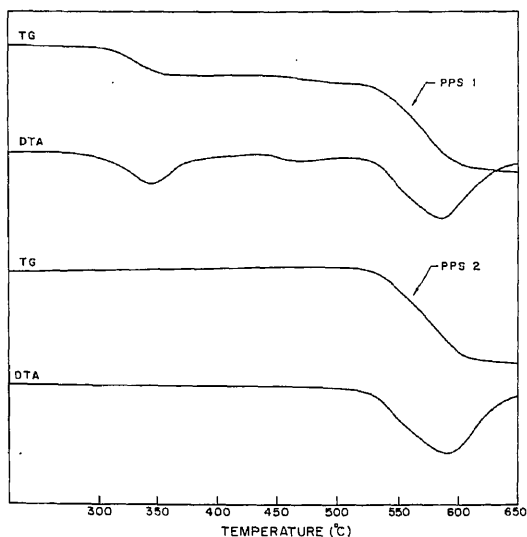


Figure 8. TGA scan for PPS samples.

ular crystallization temperature would be less for PPS 1 sample and as a result the size of the spherulites would be larger relative to the sample with higher crystallization rate. The spherulites of the two PPS samples also exhibited difference in texture. The texture of a spherulite can be defined as coarse or fine depending on the cross section of the fibrils. The spherulites of PPS 2 exhibit fine texture compared to those of PPS 1. The coarseness of the spherulitic structure for

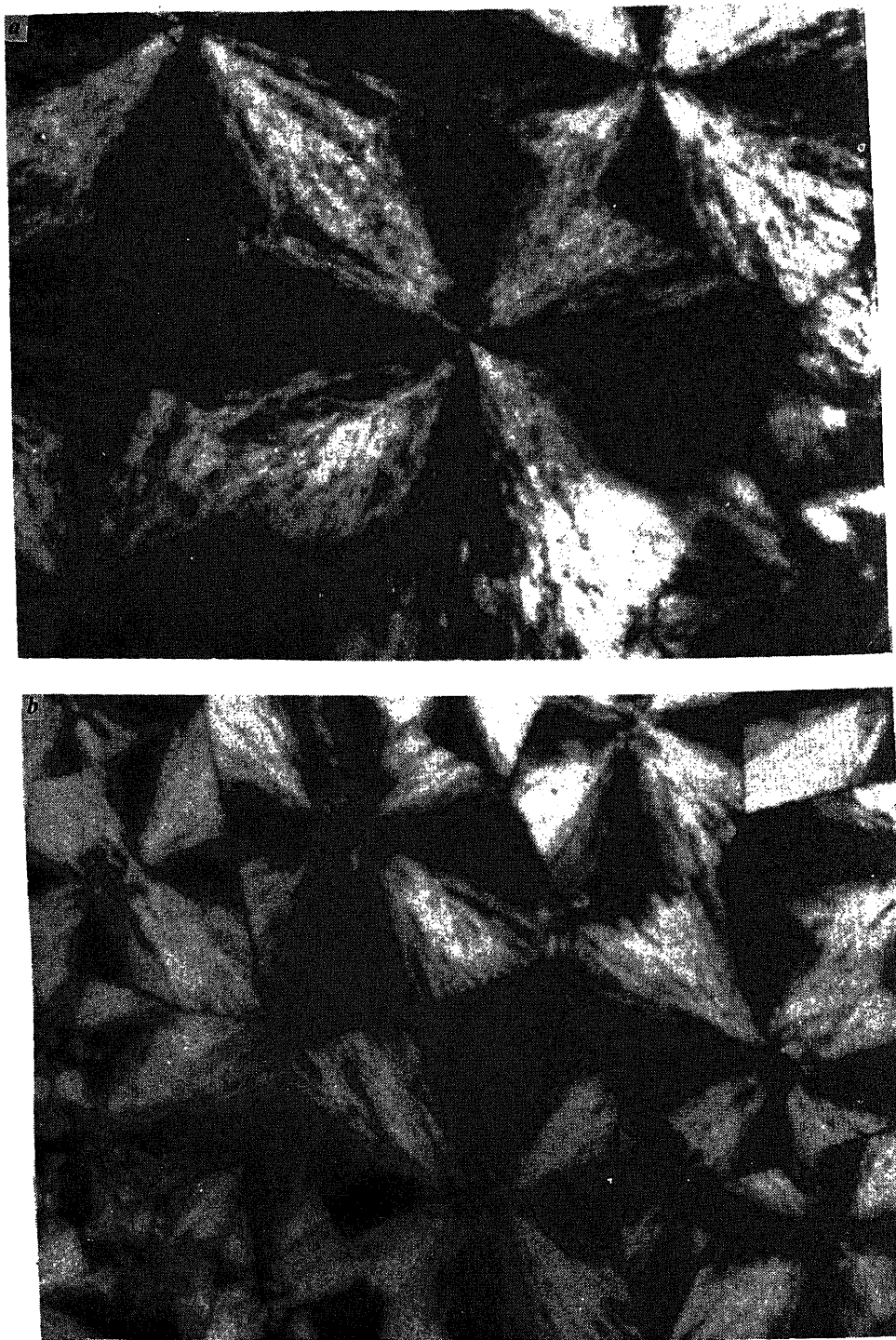


Figure 9. Optical micrographs for a. PPS 1 and b. PPS 2 samples isothermally crystallized at 235°C.

PPS 1 may be attributed to the presence of non-crystalline regions between growing fibrils (Keith and Padden Jr 1963).

4. Conclusions

The differences in the thermal and crystallization behaviour of PPS samples of different manufactures are attributed to the possible differences in the molecular architecture. The structural differences manifest themselves in terms of the depression in the equilibrium melting point, retardation of nucleation and overall crystallization rate and coarsening of spherulitic texture. The linear polymer exhibited higher equilibrium melting point, faster nucleation and higher overall crystallization rate as compared to the branched polymer. The high temperature curing behaviour also indicated similar changes in the response parameters. Thus, techniques such as TGA and nonisothermal crystallization can be used to ascertain changes in molecular architecture of polymers with the same chemical structure. Since the crystallization and curing, both these processes are important from the application point of view and a thorough study of PPS grades is required to obtain a product with desired properties.

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Thermal expansion of irradiated nylon-6 from 10 K to 340 K

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Abstract. Thermal expansion of irradiated nylon-6 has been studied in the temperature range 10 to 340 K using a three-terminal capacitance bridge technique. Irradiation is carried out using cobalt-60 γ -rays up to 500 Mrad dosage. Radiation enhances chain scission over crosslinking. α increases from 0 to 250 Mrad between 10 to 340 K and not much variation is observed between 250 to 500 Mrad for samples from 10 to 250 K.

Keywords. Thermal expansion; low temperature; γ -irradiation; nylon-6; polymer.

1. Introduction

Study of the thermal properties of irradiated polymers is very important from both scientific and technological points of view. Very little information is available on thermal properties like thermal conductivity, specific heat and thermal expansion of irradiated polymers. Thermal expansion of some of the technologically important polymers were studied after exposing the samples to high energy radiation (Subrahmanyam and Subramanyam 1987; Jayanna and Subramanyam 1992, 1993). No thermal properties are studied for irradiated nylon-6. We have made an attempt to measure thermal expansion of irradiated nylon-6 from 10 K to 340 K.

Polyamides have been exposed to a variety of high energy radiations and various physical and chemical changes have been studied by researchers and these are summarized by Zimmerman (1972). It has been observed that on irradiation crosslinking and chain scission occur simultaneously in nylon-6 and its co-polymer. These effects are due to the formation of free radicals, which are on the alpha carbon atom. Also due to the amide nitrogen and steric reasons, chain scission predominates over cross linking. Mechanical properties of nylon-6 fibres irradiated by cobalt 60 γ -ray source to the 10 Mrad level were studied by Ellison *et al* (1984). They found that the tensile strength and elongation at break of the fibre decreases with radiation dose. These effects are due to main chain scission.

Intrinsic viscosity of nylon-6 was measured by Gupta *et al* (1988) and they observed that the intrinsic viscosity $[\eta]$ first decreases and then increases for the sample irradiated in inert atmosphere. However, irradiation in air decreases the viscosity rapidly. This suggested that main chain scission occurs predominantly upon irradiation in air and chain scission and crosslinking takes place simultaneously on irradiation in inert atmosphere.

2. Experimental procedure

2.1 Material

The samples are in the form of rods as received from Polypenco (UK). The samples

are cut into required length of about 1 cm and about 1 cm diameter. The samples were irradiated with cobalt-60 γ -ray source in air at room temperature at a dose rate of 0.25 Mrad/h at the Cotton Textile Research Laboratory (CTRL), Bombay. The samples were irradiated up to 500 Mrad dosage. After irradiation the samples were continuously exposed to air.

2.2 Measurements

The melting temperatures of the unirradiated and irradiated samples were measured using Perkin Elmer DSC-2 model. Runs were conducted on samples of about 10 mg at a heating rate of 10°C/min. The melting point of nylon-6 samples with radiation dose is given in table 1.

The X-ray diffraction pattern of the irradiated samples was measured by using Philips model PW-1050/70 diffractometer with nickel filtered CuK_α radiation. The X-ray diffraction pattern was taken for the powdered sample. The diffraction pattern shows the amorphous nature of the sample. The X-ray diffraction pattern for unirradiated sample is shown in figure 1.

Thermal expansion of samples was measured by using three-terminal capacitance technique which is explained in detail elsewhere (Subrahmanyam and Subramanyam

Table 1. Melting point of nylon-6 samples irradiated to different radiation doses.

Radiation dose (Mrad)	Melting point (°C)
0	262.8
100	214.5
200	208.7
500	195.7

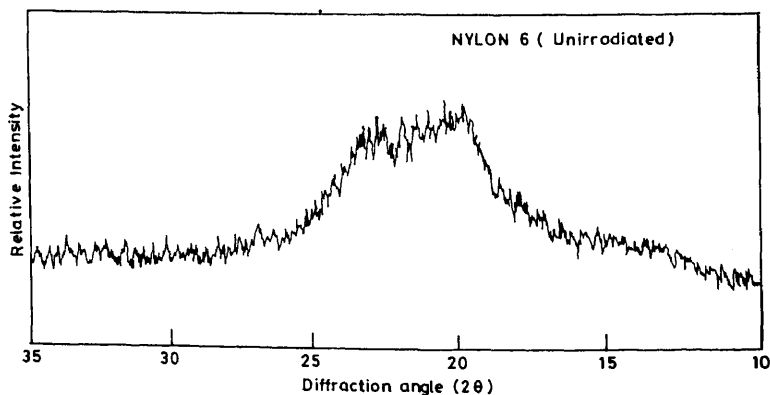


Figure 1. X-ray diffraction pattern of unirradiated nylon-6.

986). Thermal expansion coefficient (α) has been measured for nylon-6 samples irradiated to 0, 250 and 500 Mrad in the temperature range 10 K to 340 K. The variation of α with temperature is shown in figure 2. The variation of α with dose at various temperatures is shown in figure 3.

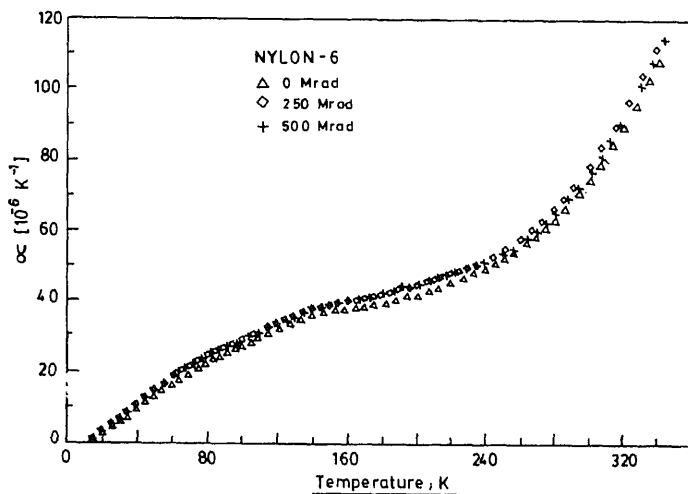


Figure 2. Variation of α of nylon-6 with temperature.

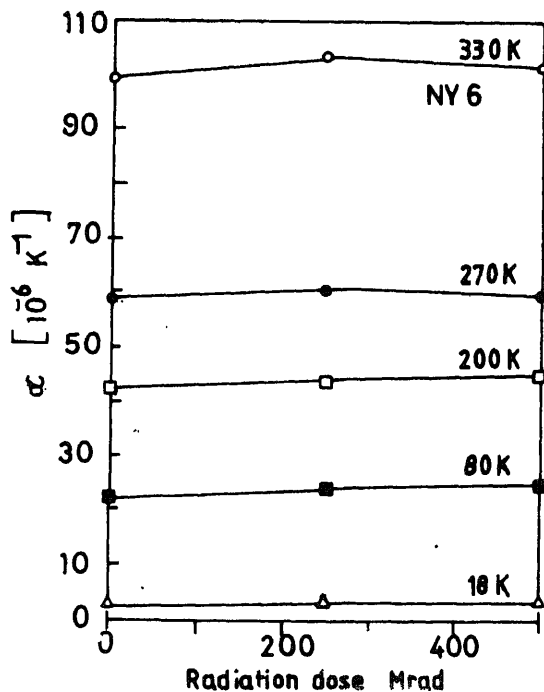


Figure 3. variation of α of nylon-6 with radiation dose.

3. Results and discussion

From table 1 it is observed that the decrease in melting point of nylon-6 samples with radiation dose is an indication of chain scission predominance over crosslinking.

From figures 2 and 3 it is observed that α increases from 0 to 250 Mrad between 10 K and 340 K, but not much variation is observed between 250 and 500 Mrad samples from 10 K to 250 K. Above 250 K, α values decrease after 250 Mrad. The increase in α is about 3% from 0 Mrad to 250 Mrad samples throughout the temperature range.

As mentioned earlier, chain scission is a predominant process in nylon-6 when it is irradiated in the presence of air. The presence of oxygen in the side group macroradicals may result in decrease in the crosslinking index. The increase in α between 0 and 250 Mrad sample is due to the degradation of nylon-6 during irradiation. For every chain scission, one van der Waal bond will arise. Since the thermal expansion is dependent on the type of interaction between the macromolecules and is large for van der Waal's type bonded solids, α increases with increasing radiation dose. This is also supported by the work of Choy *et al* (1981) and Wang *et al* (1982). The moisture, if present in the sample, is responsible for reduction in interchain interactions (Deopura *et al* 1983) and hence an increase in α .

Invariance of α for 250 and 500 Mrad samples from 10 K to 250 K is due to the competition process between crosslinking and degradation effect on thermal expansion. The decrease in α for samples irradiated to more than 250 Mrad in the temperature range 250 K to 340 K is not understood clearly.

Acknowledgements

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Effect of structure on properties of vinyl ester resins

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Abstract. The paper describes the synthesis of vinyl ester resins based on diglycidyl ether of bisphenol-A (epoxy equivalent = 450–465 g/eq) (VR resin) and tetrabromobisphenol-A (epoxy equivalent = 380–420 g/eq) (VR-1 resin). The viscosity of styrenated VR resin was higher than VR-1 resin. The effect of styrene and α -methyl styrene on curing of VR resins was studied. An increase in styrene from 30 to 50 wt% resulted in an increase in gel time and a decrease in exothermic peak. Addition of α -methyl styrene delayed and depressed the exotherm. The mechanical properties of VR resin sheets and glass fabric reinforced laminates were better than VR-1 resins; whereas LOI of VR-1 was higher. A resin formulation containing 20–30 wt% of VR:VR-1 showed optimum mechanical properties and LOI.

Keywords. Vinyl ester resin; synthesis; mechanical properties.

1. Introduction

Methacryloxy or acryloxy derivatives of epoxy resins (vinyl ester resin) are suitable materials for corrosion resistant equipments, body and structural part for land transportation vehicles, electrical insulation, radiation curable inks and coating formulations. Vinyl ester (VE) resins combine the excellent thermal and mechanical properties of epoxy resins with the ease of processing and rapid curing of polyester resins (Kay 1981). The viscosity of neat vinyl ester resins is high, thereby making processing difficult. Hence reactive diluents such as styrene, alkyl methacrylates (Yilgor *et al* 1985), α -methyl styrene are added to the resin which not only help in processing but improve some properties (e.g. strength, % elongation, hardness, chemical and scratch resistance) and brings down the cost of the resin. The effect of reactive diluent content on properties of VE resins has already been reported (Goel *et al* 1985; Varma *et al* 1985).

In our earlier studies we have reported the synthesis and characterization of vinyl ester resins based on diglycidyl ether of bisphenol-A (DGEBA) (Bhatnagar and Varma 1989; Padma *et al* 1993b) and epoxy novolac resins (Padma *et al* 1993a). The epoxy equivalent weight of the epoxy resins used were 221 (DGEBA) and 186 g/eq (epoxy novolac resin). An epoxy backbone of higher molecular weight is expected to produce greater toughness and resiliency. Therefore it was considered of interest to study the properties of VE resins based on an epoxy resin of higher molecular weight. The flame resistance of VE resins can be improved by incorporation of bromine containing compounds. The present paper reports the synthesis,

*For correspondence.

characterization and properties of vinyl ester resins based on diglycidyl ether of -bisphenol A/tetrabromobisphenol-A. The effect of reactive diluent content on the curing behaviour was also investigated.

2. Experimental

2.1 Synthesis of vinyl ester resins

The synthesis of vinyl ester resin was done in a 1 L three necked flask equipped with a condenser having a CaCl_2 guard tube. Air was bubbled through one inlet and a temperature sensor was fixed in another. 183 g of epoxy resin (Ciba Geigy) (epoxy equivalent 450–465 g/eq), 85 g of methacrylic acid (GSFC), 80 mL of methyl ethyl ketone (E. Merck), 85 mg of hydroquinone and 5 g of quaternary ammonium salt were placed in the flask, which was then heated on a heating mantle maintained at 90–100°C. The reaction was stopped when the acid number was below ten. The solvent was distilled off and the resin was cooled and stored at 10°C. This resin has been designated as VR in subsequent discussion.

The synthesis of brominated vinyl ester resin (designated as VR-1) was carried out in a similar manner using 180 g of diglycidyl ether of tetrabromobisphenol-A (Taiwan) (epoxy equivalent = 380–420 g/eq), methacrylic acid (70 g), methyl ethyl ketone (80 mL), quaternary ammonium salt (5 g) and hydroquinone (80 mg).

2.2 Characterization

The viscosity of vinyl ester resins containing different amounts of styrene (30–50 wt%) was determined using a Brookfield synchroelectric viscometer equipped with a LV-2 spindle at room temperature. The viscosity of VR : VR-1 resins (weight of VR-1 from 0–40) containing 50% styrene as reactive diluent were also determined.

Gel time determination of 50 g resin samples was done at $25 \pm 1^\circ\text{C}$ using 1 g benzoyl peroxide and 1 g N,N-dimethyl aniline (2%) at room temperature. The increase in temperature of the sample as a function of time was measured and gel time was determined by extrapolation.

2.3 Fabrication of vinyl ester resin sheets and composites

The sheets were fabricated using styrenated VR, and VR : VR-1 resin, methyl ethyl ketone peroxide (1%), N,N-dimethylaniline (0.1%) and cobalt octoate (0.1%). The requisite amount of reagents were placed in a 1L beaker and stirred using a mechanical stirrer for 30 min. After filtration (using a high vacuum pump) to remove suspended particles and degassing, the viscous syrup was poured into the toughened glass mould ($40 \times 30 \text{ cm}^2$) having PVC gasket (3 mm). The filled glass mould was then kept in an air oven at 80–90°C for 3–4 h for curing. Density of the cured sheet was determined by displacement method according to ASTM D-792, by using a Mettler electronic balance and sample of size $2.5 \times 2.5 \text{ cm}^2$.

Glass fabric reinforced vinyl ester resin composites were fabricated using hand lay up technique. Benzoyl peroxide (2%) and N,N-dimethyl aniline (0.06%) was

used as the initiator. The required quantity of vinyl ester resin, styrene and initiator were mixed in a 500 ml beaker. The total quantity of the solution was 130 g. It was then stirred using a mechanical stirrer for complete mixing and filtered. This resin solution was then brush-coated uniformly on the glass fabric of dimension $25 \times 25 \text{ cm}^2$. Ten plies were coated with the resin and stacked between steel plates covered with mylar sheets. Initial curing was done at room temperature for 24 h and then the assembly was placed between the platens of a Carver hydraulic press at $80\text{--}90^\circ\text{C}$ for 2 h (pressure 176–180 psi). Post curing of the laminates was done at 130°C for 3 h. After post curing, the laminates were machined to the required dimensions. Residual cure of resin sheets was evaluated by using a Du Pont 9900 thermal analyzer having a 910 DSC module. The resin content of the laminates was determined by heating a weighed specimen ($0.6 \times 0.6 \text{ cm}^2$) in a silica crucible in a muffle furnace at 600°C for 2 h. The glass fibre was unaffected at this temperature but the resin completely burnt off. The fibres were weighed and resin content evaluated.

Thermal stability of cured resins in nitrogen atmosphere (flow rate = $60 \text{ cm}^3/\text{min}$) was evaluated using Du Pont 1090 thermal analyzer having a 951 TG module. A heating rate of 10 K/min and sample weight of $10 \pm 1 \text{ mg}$ was used. TG traces were analyzed for (a) initial decomposition temperature (T_i) obtained by extrapolation, (b) temperature of maximum rate of weight loss (T_m) obtained from differential thermogravimetric traces and final decomposition temperature (T_f). In case decomposition proceeded in two steps, then characteristic decomposition temperature of both the steps were noted, and indicated by writing a suffix 1 or 2. The % weight loss in each step was also noted.

The limiting oxygen index (LOI) of resin sheets were determined according to ASTM D-2863. The Stanton Redcroft flammability tester was used for this purpose.

2.4 Mechanical properties of neat sheet and composites

An Instron tensile tester model 1121 was used to determine the mechanical properties. The tensile strength of specimen was determined by ASTM D-638-76. The conditions used were gauge length 7 cm, full scale load 500 kg, chart speed 200 mm/min and cross head speed 10 mm/min .

Flexural strength was measured according to ASTM D-790-71 using a three point loading system. Specimen having span-to-depth ratio of 32 : 1, width 13 mm were used. The testing conditions were: cross head speed 10 mm/min for sheets and 50 mm/min for composite, chart speed 200 mm/min , full scale load 20 kg for neat sheets and 50 kg for composite.

Inter laminar shear strength (ILSS) was determined according to ASTM-D-2344-76. The test conditions employed were: span-to-depth ratio 5 : 1, length-to-thickness ratio 7 : 1, cross head speed 1 mm/min and chart speed 100 mm/min .

3. Results and discussion

The structure of VR and VR-1 resins synthesized in the present studies can be depicted as follows:

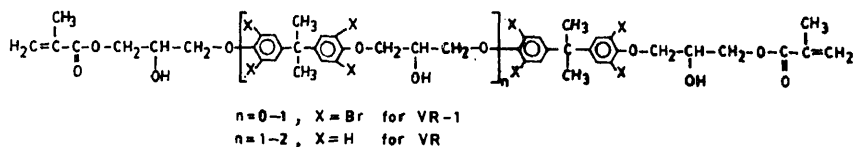


Table 1. Brookfield viscosity of styrenated VR and VR:VR-1 resins.

Resin designation	Vinyl ester resin (% w/w)		Styrene content (% w/w)	Viscosity (cps)
	VR	VR-1		
VR-A	50	0	50	15.75
VR-B	55	0	45	20.25
VR-C	60	0	40	30.50
VR-D	65	0	35	45.00
VR-E	70	0	30	78.00
VR-1A	0	50	50	5.75
VER-P	40	10	50	13.00
VER-Q	30	20	50	11.00
VER-R	25	25	50	10.25
VER-S	20	30	50	9.25
VER-T	10	40	50	7.25

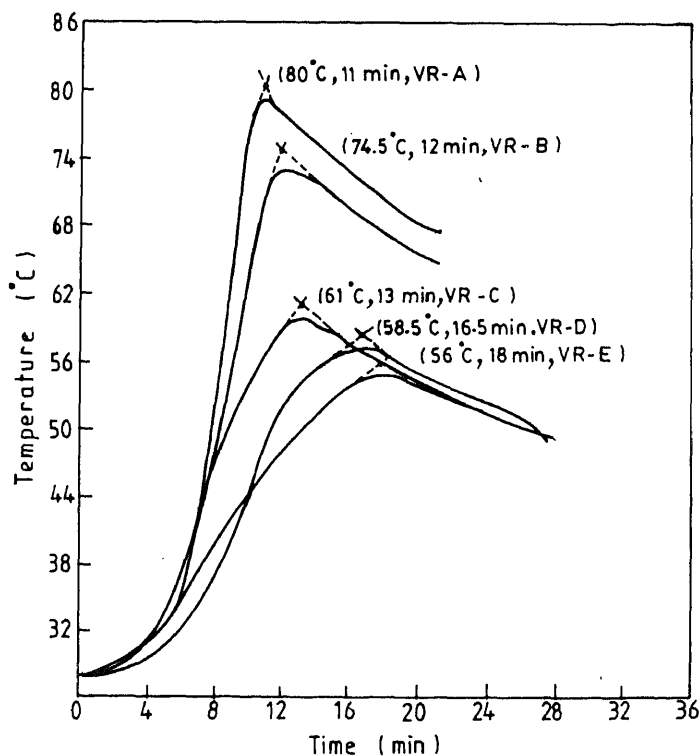


Figure 1. Gel point determination of VR resin in presence of different wt% of styrene (initiator benzoyl peroxide and *N,N*-dimethyl aniline).

Table 2. Effect of α -methyl styrene (α -MS) on cure characteristics of styrenated vinyl ester resin.

VR (%, w/w)	Styrene (%, w/w)	α -MS (%, w/w)	Gel time (min)	Exotherm peak temp. ($^{\circ}$ C)
50	50	0	18	56
50	48	2	20	51
50	45	5	22	43
50	40	10	> 8 h	—

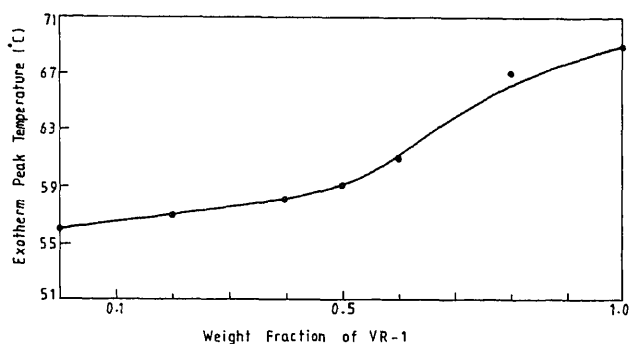
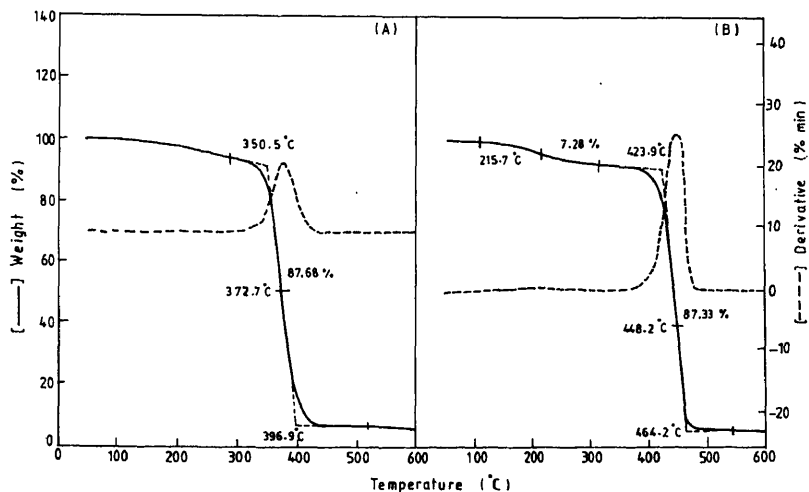
**Figure 2.** Effect of VR-1 content on exotherm peak temperature of VR:VR-1 resin formulation containing 50 wt% of styrene (initiators-benzoyl peroxide and N,N-dimethyl aniline).**Figure 3.** TG traces of (A) VR-1A and (B) VR-A resin sheets in N_2 atmosphere.

Table 3. Thermal behaviour of cured vinyl ester resin sheets.

Decomposition temp. (°C) (% wt loss)	VR-A	VER-P	VER-R	VER-T	VR-1A
T_{i1}	160	170	168	150	—
T_{m1}	215	230	223	226	—
T_{f1}	315	290	270	270	—
(% wt loss)	(7.3)	(6.9)	(6.3)	(5.0)	—
T_{i2}	424	377	336	356	350
T_{m2}	448	415	389	378	372
T_{f2}	464	437	410	404	397
(% wt loss)	(87)	(87)	(81)	(88)	(87.7)

Table 4. Mechanical properties of cured vinyl ester resins.

Resin designation	Property				
	TS (MPa)	TM (GPa)	FS (MPa)	FM (GPa)	Limiting oxygen index (%)
VR-A	30.78	1.05	78.18	3.42	19.9
VER-P	30.56	1.32	77.83	3.57	20.8
VER-Q	34.08	1.53	76.88	3.57	21.2
VER-S	35.95	1.45	75.76	3.69	22.4
VR-1A	34.81	1.48	67.70	3.55	23.0

Table 5. Mechanical properties of vinyl ester resin composites.

Resin designation	Property			
	Resin content	FS (MPa)	FM (GPa)	ILSS (MPa)
VR-A	37.71	377.16	21.96	38.42
VER-P	37.25	418.80	21.28	39.79
VER-R	38.09	353.92	21.05	33.33
VER-T	40.37	308.72	20.24	26.71
VR-1A	39.20	323.12	20.51	28.68

The viscosity of VR containing different weight% of styrene and of VR : VR resin containing 50 wt% of styrene are given in table 1. As expected, the viscosity of VR resin decreased by increasing styrene content in the formulation. The viscosity of VR-A resin (containing 50 wt% of styrene) was almost three times that of VR-1A resin (50 wt% styrene).

Gel time determination studies of VR resin in presence of different weight fraction of styrene are shown in figure 1. An increase in styrene content resulted in an increase in gel time and a decrease in exotherm peak temperature. Styrene, being a monofunctional monomer, reduces the cross-link density, thereby increasing the time for onset of gelation. A decrease in exotherm peak temperature and an increase

n time of gelation was observed by partial replacement of styrene in VR-A resin by α -methyl styrene (α -MS) (table 2).

Therefore from the gel time studies, it can be concluded that the gelation is reduced in presence of α -MS. The lower reactivity of α -methyl styrene may be explained on the basis of the greater stability of the tertiary propagating radical and hence reduced tendency for propagation.

The gel time decreased from 18 to 14 min by addition of VR-1 resin to VR (styrene content 50 wt%). The exotherm peak temperature increased from 56°C to 59°C (figure 2).

The density of cured specimen of VR-A and VR-1A were found to be 1.115 g/cm³ and 1.25 g/cm³ respectively.

The DSC scans of neat resin sheets showed absence of exothermic transition indicating thereby the absence of residual monomers/oligomers in the cured samples. These samples were stable up to 200°C. A weight loss of 5–8% was observed above this temperature (figure 3). However the major weight loss was above 420°C in VR-A and above 350°C in VR-1A. The lower decomposition temperature in VR-1A is due to the scission of C–Br bond which is thermally labile. The TG results of various resin samples are summarized in table 3.

The mechanical properties and oxygen index (LOI) of the neat sheets are given in table 4. The tensile strength of VR-1A was higher than VR-A. The tensile strength and LOI of VER-Q and VER-S resin formulation were found to be better than VR-A. Flexural strength of VR-A was higher than VR-1A. This may be due to high molecular weight epoxy resin used for the synthesis of VR-A resin. The limiting oxygen index of VR-1A was highest and it decreased by increasing VR-A content in the formulation. These results thus indicate that VER-Q and VER-S resins have good mechanical properties and flame resistance.

The glass fabric reinforced VR samples having 38.5 $\pm$ 1.5% resin, exhibited good properties (table 5). The flexural strength, flexural modulus and ILSS was higher in VR-A. An increase of VR-1A in the resin formulation resulted in a decrease in ILSS and flexural properties.

Thus the vinyl ester resin based on high molecular weight epoxy resin have better flexural strength and modulus. Addition of 20–30 wt% of brominated vinyl ester resin to this VR resin increases the LOI without affecting the mechanical properties.

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Some concepts on design of surfactant gels and vesicles

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Abstract. It is conjectured that anionic-cationic surfactant combination can be regarded as equivalent to a double chain surfactant and using molecular packing considerations it is shown that vesicles, viscoelastic solutions and liquid crystals can be designed by the proper choice of chain lengths of the pair. Using these concepts new systems are designed, from mixtures of cetyltrimethyl ammonium bromide and sodium alkyl sulfonates, to produce both viscoelastic gels and vesicles.

Keywords. Vesicles; gels; surfactants; viscoelasticity.

1. Introduction

Dilute aqueous surfactant solutions are known to assume various structures like spherical micelles, cylindrical micelles, disc like micelles, tubules etc. and design of these are of interest to a number of applications in detergent, paint, drug delivery and other industries (Fendler 1982). Classic work of Tanford (1972), Israelachvili, *et al* (1976) and others (Nagarajan 1986) identified that the key parameter is the ratio of the volume of the hydrophobic chain v to the product of length l of the chain and the area a of the polar head i.e., v/al . It has been shown that

$v/al = 1/3$ for spherical micelles,

$1/3 < v/al < 1/2$ for cylinders,

$v/al > 1/2$ for disc or vesicles.

These considerations can act as convenient guidelines and surfactants can be designed to produce these structures. Some of the examples are using salt to convert spherical to cylindrical micelles (Mysels and Princen 1959) or use of double chain surfactants to produce vesicles (Bangham 1965) or nematic liquid crystals (Hertel and Hoffmann 1984). Recently Kaler *et al* (1989) introduced a novel concept of combining a cationic and an anionic surfactant to spontaneously produce vesicles. Their results also showed that the charge on the vesicles can be controlled by this method of preparation. This aspect could be of great interest in cases where one needs a specific binding to charged surfaces. Their phase diagram also showed that the coulomb interaction between the vesicles plays an important role.

The present paper originated from the observation that the charge effects play a decisive and dominating role in obtaining viscoelastic gels of cylindrical micelles (Mishra *et al* 1993) and that the ideas which led Kaler *et al* (1989) for vesicles can be extended to viscoelastic gels too. Viscoelastic surfactant solutions have been

reviewed in an excellent article by Rehage and Hoffmann (1991) recently which gives an exhaustive review of the experiments and a summary of available understanding of the subject. Some of the main characteristics which are exhibited by a number of systems but not understood are: (a) The zero shear viscosity of CTAB or other cationics shows two peaks as the additive such as sodium salicylate is added, (b) the minimum in the viscosity between the two peaks occurs approximately at 1:1 ratio of the two components or at slightly higher values of the concentration of the aromatic additive, (c) very often phase separations occur in the region between the two peaks and in some cases liquid crystalline phases occur in addition to phase separations (Rehage and Hoffmann 1991; Mishra *et al* 1993) and (d) the rise in viscosities are sensitive to the ortho, meta para positions of the groups present in the additive molecules like salicylate (e.g. figure 5 of Rehage and Hoffmann (1991)).

The review remarks 'In terms of these observations, the explanation of the second viscosity maximum is still an unsolved problem'. The main difficulty in rationalizing the characteristics listed above has been due to the non realization of the fact that the molecules like sodium salicylate (SS) are surface active—though to a small extent (Balasubramanian *et al* 1989). The sodium salicylate molecule is having two polar groups viz. the COONa and the OH group both of which have an affinity for water and lie on one half of the molecule. The other half is almost like benzene and therefore there is a clear separation of the polar and the non polar parts. Therefore SS acts like a surface active molecule with a small hydrocarbon portion. This assertion has been verified by a number of experiments (Balasubramanian *et al* 1989), and has also been shown to have the property of hydrotropy. Once this fact is realized several things follow as a natural consequence. The main point being that CTAB-SS mixed systems should be looked upon as solutions of mixtures of cationic-anionic surfactants, the anionic with a short hydrophobic part. The specificity effects observed with respect to ortho, meta and para positions of hydroxyl group in salicylate systems are simply a consequence of the surface activity of the molecule. The most surface active species would be the SS with OH group in ortho position next would be the meta and the least surface active would be the para hydroxybenzoate and this is reflected as specificity of the viscoelasticity in these systems (Rehage and Hoffmann 1991). The realization that surface activity of SS like molecules is the key feature in causing the viscoelasticity implies that there would be a whole class of additives which could induce viscoelasticity.

2. The model

The main contention of the present paper is to extend and confirm the above observations by demonstrating that by suitable mixing of cationic and anionic surfactants of different chain lengths one can obtain viscoelastic gels or vesicles. The main governing principle being the packing considerations mentioned above. It is known that the l and v parameters for an alkyl surfactant are given by

$$l = 1.265 n + 1.5 \text{ \AA}, \quad (1)$$

$$v = 26.9 n + 27.4 \text{ \AA}^3, \quad (2)$$

where n is the number of carbon atoms in the alkyl chain. Since both l and v are linear in n , the ratio v/la for a given polar head will approach $\sim 2l/a$ for large n

and therefore there is not much option to vary the parameter v/al to obtain different structures mentioned above by varying the chain length. On the other hand if one considers a mixture of cationic and anionic surfactants then each cationic-anionic pair would in effect act as a double chain surfactant. If we assume that the cationic surfactant has a longer chain length l_0 and a volume v_0 and further, if the combination of cationic-anionic has a polar head area a , then the parameter for this combination can be written as

$$v/la = (v_0/l_0a) (1 + v_1/v_0), \quad (3)$$

where v_1 is the volume of the smaller surfactant—the anionic surfactant—and it is assumed that the length of the surfactant is decided by the longer surfactant. If one assumes that the factor in the first bracket in (3) is approximately 1/9, as is for spherical micelles, then by choosing the volume v_1 of the anionic surfactant one can vary the ratio in (3) over a fairly wide range to obtain a variety of structures. These arguments will obviously hold good when the longer surfactant is anionic and the cationic is shorter. The work of Kaler *et al* (1989) on vesicles is an example of this for $v_1 \approx v_0$. By choosing v_1 such that $0 < v_1 < 0.5v_0$ one can, in principle, obtain cylindrical structures. In fact, such examples, though not realized, exist in literature. Barker *et al* (1974) obtained viscoelastic solutions by mixing $C_{12}TAB$ and SDS. The well studied example of cationic surfactant and sodium salicylate (Hoffmann *et al* 1985) is another example though the latter is not an alkyl chain.

In the present report we demonstrate the principle of mixing two surfactants of opposite charge to produce various structures by choosing cetyltrimethyl ammonium bromide as the long chain cationic and sodium heptylsulfonate (SHS), sodium octyl sulfate (SOS) and sodium decylsulfonate (SdeS) as the short chain anionic surfactants. It is interesting to observe that (1), (2) and (3) predict that CTAB-SHS and CTAB-SOS should contain cylindrical micelles but CTAB-SdeS should form vesicles. We confirm these effects below.

3. Results

Figure 1 shows the zero shear viscosity measured as a function of the concentration of SHS for a fixed concentration of 60 mM of CTAB. These samples apart from being viscous showed viscoelastic effects like recoil of trapped air bubbles. The double peak nature of the figure is characteristic of these cationic-anionic mixture systems (for example, see, Rehage and Hoffmann (1988)) and arises from the fact when one varies the relative ratio one in fact is really varying the charge Z on the aggregates. In view of this variation of Z all the properties, like viscosity, phase diagram etc. which depend on the coulomb repulsions start showing symmetry about $Z=0$ because these effects depend on Z^2 —not on the sign of Z . This is the reason why Kaler *et al* (1989) observed two lobes of vesicular regions and lamellar phases. Similarly the double hump in the viscosity observed by Hoffmann *et al* (1985) is again the result of this effect. The observation of a two-phase region between the two peaks in the viscosity is also a result of reduced coulomb interaction. Recently Mishra *et al* (1993) observed two viscoelastic and two nematic liquid phases symmetrically placed about the two phase region in their experiments. Also the results of Barker *et al* (1974) conform to this rule. Figure 2 shows similar double peaks in viscosity of CTAB-SOS system. These examples clearly show the validity

VISCOSITY MEASUREMENTS (25 °C)

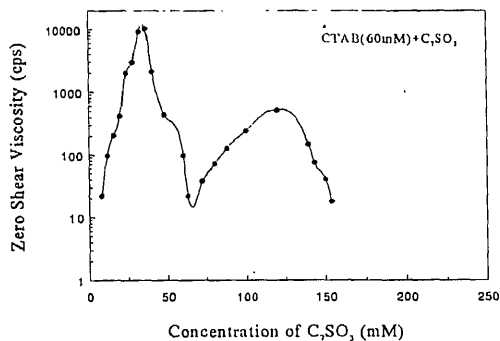


Figure 1. Viscosity extrapolated to zero shear rate of CTAB solution as SHS is added. The CTAB concentration was fixed at 60 mM. The double peak in viscosity is similar to the ones reported by Rehage and Hoffmann (1988). These samples also showed strong viscoelasticity and flow birefringence.

VISCOSITY MEASUREMENTS (25 °C)

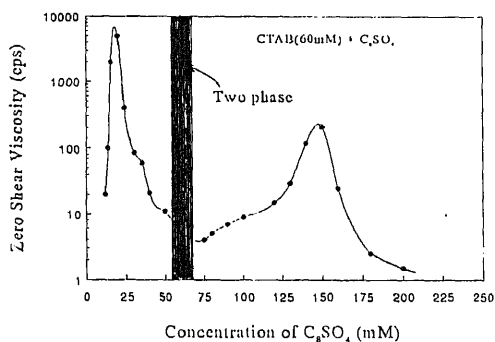


Figure 2. Viscosity of CTAB-SOS system. The presence of two peaks similar to figure 1 and others mentioned in Rehage and Hoffmann (1991) confirms that this is due to surface active nature of additive to CTAB.

of the concepts mentioned above.

The system of CTAB-SDeS formed turbid solutions. The dynamic light scattering results, using Brookhaven Instruments model BI-90, indicated that these solutions consisted of a suspension of particles of diam 150 nm. These results were indicative of the existence of vesicles. Normally one adds Triton X-100 to break vesicles and this worked in our case too. Turbidity of the solutions disappeared on addition of Triton X-100 and the solutions were clear. A fluorescent dye carboxy fluorescein solution was prepared and the two surfactants CTAB and SDeS were added to the solution to produce turbid solutions again. This mixture was dialyzed to remove the dye outside the possible vesicles. The fluorescent intensity decreased, self absorption

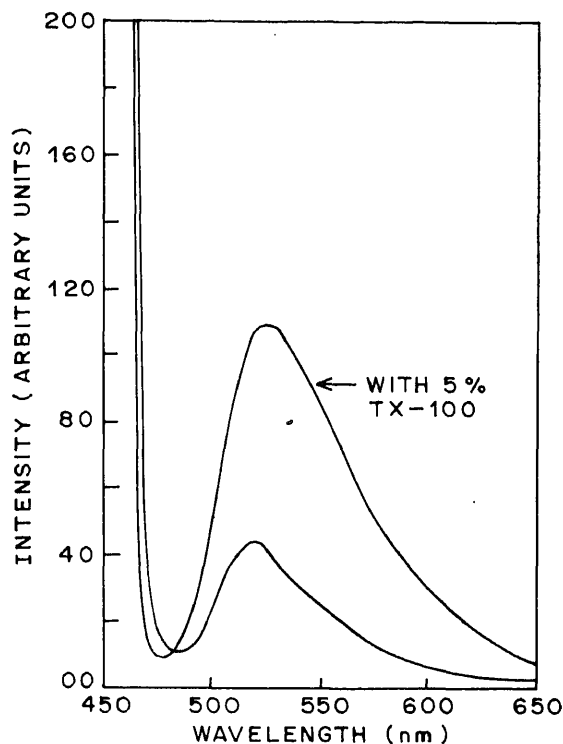


Figure 3. Fluorescence intensity of carboxy fluorescence (CF). Excitation at 450 nm. The low intensity band is from CF trapped in vesicles. On adding Triton X-100 the vesicles break and release the trapped CF and the intensity is enhanced.

being the only mechanism for the dye concentrate trapped inside the vesicles. On breaking the vesicles by addition of Triton X-100 the fluorescence intensity increased indicating the release of the dye. Figure 2 shows the enhancement observed confirming the presence of vesicles. The existence of vesicles is also expected in view of the similarity of the system with that of systems investigated by Kaler *et al* (1989).

Addition of SdeS to a solution of CTAB with constant concentration of 60 mM also produced two vesicular phases and the transitions

Turbid (vesicles) $\rightarrow$ 2-phase $\rightarrow$ turbid (vesicles),

again indicating the importance of coulomb effects and similarity with the results of Kaler *et al* (1989).

4. Conclusions

These results clearly indicate that the approach initiated by Kaler *et al* (1989) for vesicles is flexible and can be extended to viscoelastic solutions and possibly to liquid crystalline systems. These results also indicate that with the combination of

two concepts, viz. the surface activity of the additives like SS, SHS etc. and the coulomb interaction between the aggregates the main characteristics of the viscoelastic solutions mentioned above can be rationalized at least qualitatively.

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Physical characterization of the organic nonlinear optical crystal – 3-methoxy 4-hydroxy benzaldehyde

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Abstract. We highlight our recent experimental work on an efficient molecular nonlinear optical crystal, 3-methoxy 4-hydroxy benzaldehyde (MHBA). Optical quality single crystals of MHBA were grown from mixtures of solvents and from melt. The overall absorption and transparency window were improved by growing them in a mixture of chloroform and acetone. The grown crystals were characterized for their optical transmission, mechanical hardness and laser damage. We have observed a strong correlation between mechanical properties and laser induced damage.

1. Introduction

High storage density optical devices require laser sources at short wavelengths, typically around the blue region. Direct compact sources are currently not available at these wavelengths. A viable alternative is to obtain them by intra-cavity frequency doubling of GaAs-AlGaAs lasers. The requirements for such crystals are very stringent; they should have high nonlinearity, high angular acceptance and high damage threshold. Till today the only inorganic crystal in which intra-cavity frequency doubling of GaAs lasers was demonstrated is KNbO_3 . However, this requires thermal stabilization of the cavity as the thermo-optic coefficients of KNbO_3 are high, which is a serious handicap in device fabrication. Hence alternative materials are currently being explored, and 3-methoxy 4-hydroxy benzaldehyde promises to be a good candidate. MHBA is an efficient molecular nonlinear optical (NLO) material. It has relatively weak donor and acceptor ($-\text{CHO}$ and $-\text{OH}$) at para positions in a benzene ring and $-\text{OCH}_3$ group attached at the meta position, ensuring an acentric crystal structure. Its SHG powder efficiency is as high as 30 times that of urea and it has transparency in the blue region. It has a low threshold for SHG and low angular sensitivity. Also, crystals of MHBA can be grown from solutions at low temperature. A combination of these desirable properties makes MHBA an excellent material for investigation as a frequency doubler for GaAs lasers. In this paper we discuss some of our recent experiments on this important organic NLO crystal.

2. Experimental and results

2.1 Crystal growth

Single crystal of MHBA were grown from various solvents and solvent mixtures using an indigenous growth unit fabricated in our laboratory (Dhanaraj *et al* 1991). It was observed during our growth experiments that MHBA, owing to its highly polar nature,

grows as needles and rods from various solvents. Hence single crystals were grown from various solvent mixtures. The results of our extensive investigations on the effect of solvent and solvent mixtures on the crystal habit and optical quality of MHBA have already been published in one of our earlier papers (Venkataramanan *et al* 1994a).

Since it was very difficult to grow large single crystals of MHBA from solvents or solvent mixtures, we considered it worthwhile to attempt other methods of growth as well. As a first step towards melt growth, we studied the behaviour of MHBA at the melting point. Our DSC (figure 1) and TGA experiments showed that the compound does not sublime and is quite stable up to its melting point. These results indicated that MHBA could be grown from melt. Subsequently, large single crystals of MHBA of size $30 \times 20 \times 2 \text{ mm}^3$ were grown from melt (figure 2). In general, the melt grown crystals were yellowish in colour indicating increased optical absorption. However, unlike the solution grown crystals, these crystals did not suffer from inclusions and their preferential incorporation into certain regions (Venkataramanan *et al* 1994a).

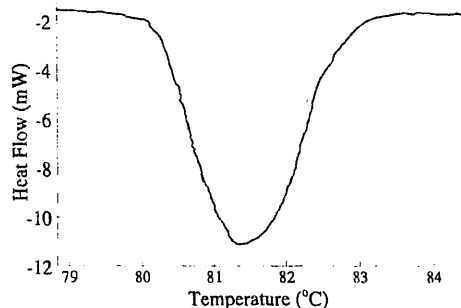


Figure 1. DSC curve of MHBA.



Figure 2. Photograph of a typical melt grown crystal.

2.2 Optical transmission

Molecular NLO crystals usually have high absorption in the visible wavelength and narrow transparency window. This is one of the disadvantages of these materials which limits their utility. The high excited-to-ground state dipole moment that increases the nonlinearity also increases the absorption. MHBA, however, has only weak donor and acceptor and hence can be expected to have lower absorption than the other organic crystals.

Figure 3 shows the optical transmission of MHBA in the region 200–2000 nm. MHBA was found to have low absorption at the Nd:YAG fundamental wavelength, which contributes to its resistance to laser induced damage. Also, there was very little absorption at the doubled wavelength (532 nm), which can improve the second harmonic throughput. It was also found to have an extended transmission range (down to 360 nm). This, coupled with the high nonlinearity makes MHBA very attractive for diode laser frequency doubling applications as well as those with tunable Ti-sapphire lasers.

On visual examination, the crystals grown from chloroform-acetone mixture were found to be less coloured than those from acetic acid-water mixture. Optical absorption studies were hence carried out on samples grown from different solutions, which yielded crystals large enough for characterization. Particularly, crystals grown from acetic acid-water and chloroform-acetone were chosen for comparison. The inset in figure 3 shows the low wavelength cut-off of the crystals grown from acetic acid (370 nm) and those from chloroform mixtures (365 nm). It was observed that in samples of identical thickness, the crystals grown from chloroform-acetone mixture had approximately 10% less absorption than those grown from the other mixture. It should be emphasized here that though the mixture of acetic acid-water gave larger crystals (Zhang *et al* 1992), crystals grown from chloroform-acetone mixture, with higher transparency range and low overall absorption are more suitable for optical experiments. As regards to the melt grown crystals, there was an overall

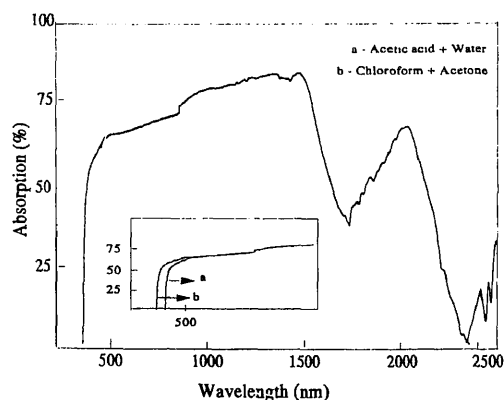


Figure 3. Optical transmission of MHBA crystals grown from chloroform-acetone mixtures. The inset shows the increase in transparency when compared to the crystals grown from acetic acid-water mixture.

increase in optical absorption as compared to those grown from solutions. Further optimization of the growth conditions is required to improve the optical transmission in the melt grown crystals.

2.3 Defects characterization

The grown MHBA crystals were characterized for defect content using topography employing the synchrotron radiation source at Daresbury Laboratory, UK. The surface damage from cleavage was removed by wet polishing the crystal. The crystal plate of 2 mm thickness was set to 400 reflection for 0.72 Å radiation of the white radiation from a synchrotron source. Figure 4 shows a typical synchrotron topograph of a MHBA crystal grown from chloroform-acetone mixture. In general, the dislocation densities were very high, as the crystals were self-nucleated. Consequently, the individual dislocations could not be resolved. This topograph reflects the typical characteristics of organic crystals, showing high contrast variations and poor resolution (Halfpenny *et al* 1993).

Figure 5 is the synchrotron topograph of a MHBA crystal grown from melt. As can be seen from the figure the melt grown crystals were highly strained. As a result of the large strain, some regions of the topograph are seen in out of diffraction conditions, which results in an incomplete imaging of the crystal. An improvement in the overall quality should be possible with improved growth conditions. This work is currently under progress to optimize the growth conditions.

2.4 Laser induced damage

Previous report on laser damage indicated a threshold value in excess of 1 GW/cm² for MHBA for a 25 ns pulse (Yakovlev and Poezshalov 1991). However, they were unable to accurately measure the damage threshold of MHBA. Hence, a measurement of laser damage resistance was made on the MHBA crystals grown from solution.

For laser damage experiments a picosecond Continuum YG601 Nd:YAG laser was used.

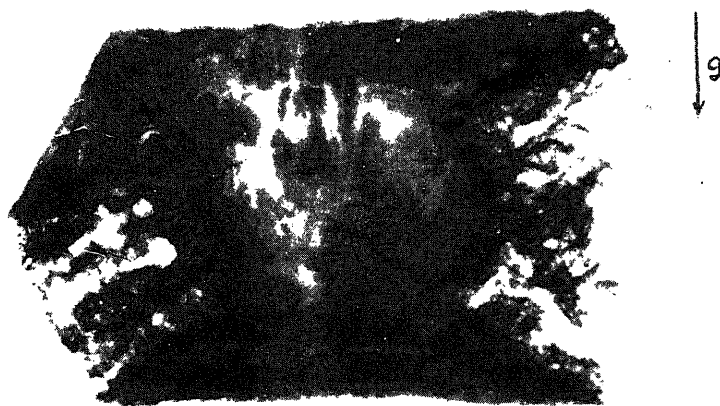


Figure 4. Synchrotron topograph of MHBA crystal grown from solution, $\lambda = 0.72$ Å, 400 reflection, 001 plate.

was used. The experimental set-up for evaluating laser induced damage is shown in figure 6. The combination of polarizer and the attenuator serves to cut the input intensity to the required level. The beam splitter transmits 15% of the power to the pyroelectric probe (Laser Precision Corporation, RjP-7735). The power meter was triggered by synchronous pulses from the Q-switch of the Nd:YAG laser. The crystals were kept slightly away from the focal spot of the beam. A low power He-Ne laser beam was also simultaneously focussed onto the crystal. When damage occurs, this He-Ne beam gets scattered which could easily be detected even by naked eye. The transmitted He-Ne beam from the crystal was collected on a screen for further facilitating the detection of damage occurrence.

MHBA samples were prepared by cleaving the crystals in the (001) plane. As



Figure 5. Synchrotron topograph of MHBA crystal grown from melt. $\lambda = 0.72 \text{ \AA}$, 400 reflection, 001 plate.

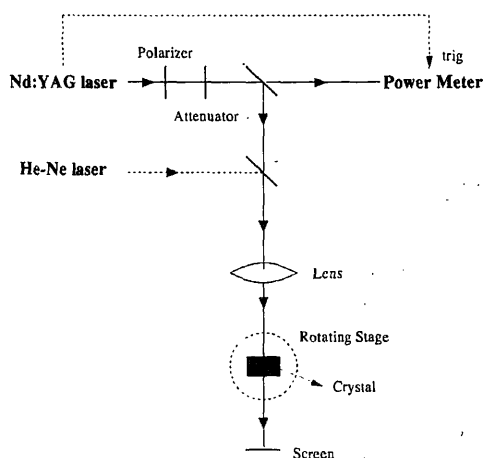


Figure 6. Experimental arrangement for laser damage measurements.

the cleavage was facile and smooth without any steps, no polishing was required. No special cleaning was done to the surface. The crystals selected for the experiments were of the best quality among those grown. Since MHBA crystals always grow with inclusions in negative b axis, exposures were restricted to the other end. Pre-exposure examination in selecting the test site included visual examination for inclusions and looking for light scattering from the He-Ne laser used as the probe in the actual experimental arrangement.

During single shot experiments to measure 1-on-1 (P_1) damage resistance values, the laser was operated by a remote control. The occurrence of damage (or otherwise) was monitored on the screen and irrespective of whether the damage had occurred or not, the samples were moved to a new site. The distance between the two sites was kept at least 5 times the spot size on the crystal surface.

During multiple shot experiments n -on-1 (P_n), the laser beam at sub-threshold value was made to fall on same site of the crystal and the onset of damage (the scattering of He-Ne beam) was monitored on the screen. The laser power was continuously monitored and averaged for the entire duration of the experiment. If the damage had not occurred even after 2000 pulses, the crystal was moved so that the beam fell at a new site and the experiment was repeated with slightly higher power. This procedure was repeated till the test site was damaged with 2000 pulses. The value of P_n was averaged over a large number of observations.

The laser parameters and the results obtained are given in table 1. It can be seen that the damage threshold values obtained during the present investigations are less than that reported earlier, considering the fact that the present study is with picosecond pulses. In their experiments, Yakovlev and Poezzhalov (1991), had kept the crystals in an evacuated chamber with quartz windows. It was not clear if they had accounted for the absorption in the quartz window while calculating the total power at the crystal surface. Also, it was not explicit whether their experimental values corresponded to the bulk damage measurements, in which case it can be an order of magnitude higher than the surface threshold. During the present investigation, the crystals were directly exposed to focused radiation without any enclosures and the values reported here are for surface damage threshold.

Table 1. Laser damage in MHBA—Test parameters and results.

Test parameters	
Wavelength	532 nm
Repetition rate	5 Hz
Pulse width	32 psec
Beam profile	TEM ₀₀
Beam diameter	3.6 mm (at $1/e^2$)
Specimen orientation	(001)
Polarization	perp. to b
Results	
Single shot (P_1)	7 GW/cm ²
Multiple shot (P_n)	0.8 GW/cm ²

2.5 Mechanical hardness

It was speculated previously that a knowledge of the mechanical properties of NLO crystals is essential in understanding the origin of laser induced damage in them (Yokotani *et al* 1989). With this in view, we carried out mechanical hardness studies on these crystals. The anisotropy of hardness of MHBA was evaluated on the cleavage (001) plane by Knoop indentation. A Leitz Miniload tester fitted with a Knoop indenter was used. A constant load of 15 g was applied for all indentations. The descending time was kept constant at 20 sec and the dwell time 40 sec. Starting from the *a* axis, indentations were made for incremental rotations of 10° in the entire (001) plane and the KHN were averaged over a large number of values. Figure 7 shows the variation of mechanical hardness as a function of angle. As can be inferred from the graph, there is a marked anisotropy in hardness of MHBA. Hardness along *b* axis is higher than that along the *a* axis. In general, the hardness of MHBA is quite lower when compared to those of inorganic NLO crystals. The lower hardness value can be attributed to the presence of relatively weak bonds in the MHBA molecule. The information on hardness anisotropy was subsequently used in understanding the nature of laser induced damage in the crystal, as outlined below.

The morphology of the damage pattern can reveal the nature and possible origin of damage in the crystals. The damage patterns often reflect the symmetries of the crystal surface. Earlier workers have predicted the origin of laser damage through a careful examination of these patterns, which included dielectric breakdown, thermal decomposition, etc (Ellenberger *et al* 1992; Bolt and van der Mooren 1993). However, no specific correlation between the mechanical hardness anisotropy and the nature of laser damage has been made so far. To observe the possible correlation, we examined the morphologies of laser induced damages in MHBA and compared them with mechanical hardness anisotropy. Post-exposure examination of the damaged surfaces revealed highly anisotropic damage profiles, the orientation of which were identified from the morphology of the samples. The elliptical laser damage has its major and minor axes along the crystallographic *b* and *a* axes (figure 8a). The polar plot of hardness anisotropy (figure 8b) was compared with the damage morphology.

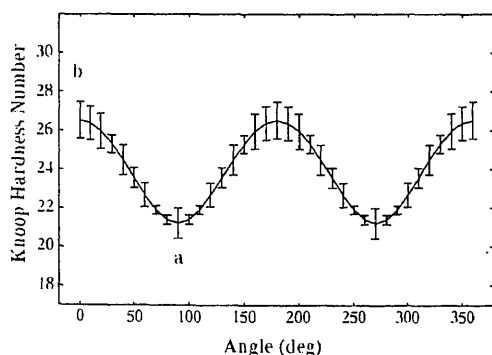


Figure 7. Mechanical hardness anisotropy of MHBA in the (001) plane.

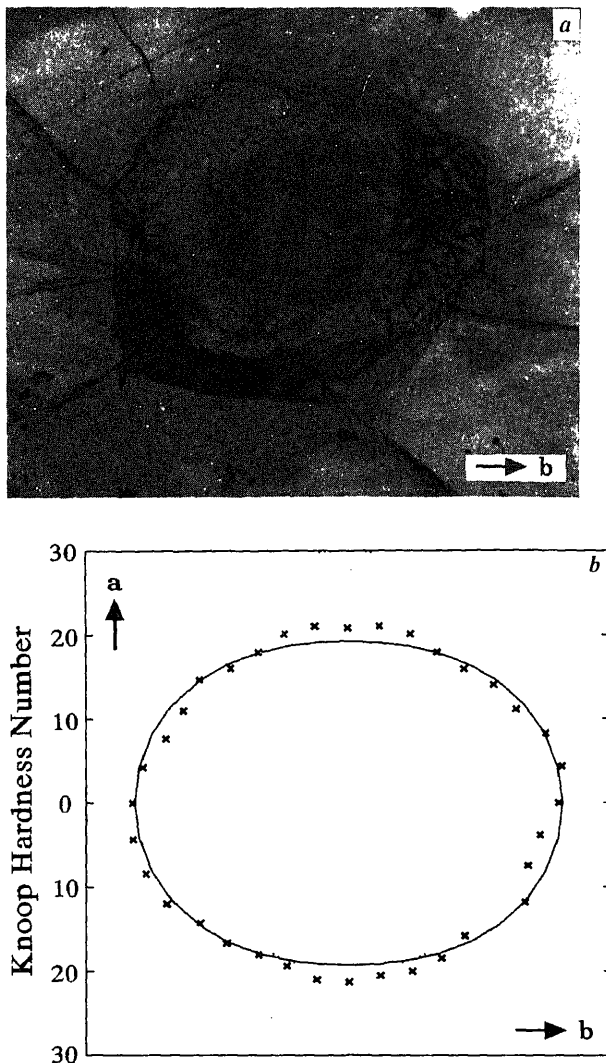


Figure 8. a. Optical micrograph of laser induced damage in 001 plane of MHBA ($\times 60$) and b. polar plot of hardness anisotropy of MHBA.

It was observed that the laser damage was severe along the mechanically harder b axis. This is in consistence with our reports on other NLO crystals, viz. L-arginine phosphate monohydrate (LAP) (Venkataramanan *et al* 1994b) zinc tris(thiourea) sulfate (ZTS) and bis(thiourea) cadmium chloride (BTCC) (Venkataramanan *et al* 1994c). However, unlike the other crystals studied by us, MHBA has a sharp damage threshold value. Just above the threshold there were severe fragmentation and fracture, leading to the physical removal of material from the surface. We attribute this to the presence of a facile cleavage plane in MHBA. It should, however, be reiterated that the mechanism of laser induced damage is highly complicated and case-specific. Detailed studies are warranted on different crystals under identical experimental conditions to develop a comprehensive model.

3. Conclusions

Single crystals of MHBA were grown from various solvents, solvent mixtures and melt. Spectrophotometric studies on single crystals revealed that crystals grown in a mixture of chloroform and acetone have lesser absorption than those grown from other solvent mixtures. Also crystals from chloroform-acetone have increased transparency window and are thus better suited for optical applications. Detailed thermal analysis on the compound revealed that MHBA does not have any high temperature phase transition and does not sublime appreciably till its melting point. Mechanical hardness assessment on MHBA indicates that the crystals are softer than semiorganics. Laser damage threshold experiments revealed a high resistance to laser damage and the damage morphologies were found to have strong correlation with mechanical hardness anisotropy.

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Electroclinic measurement of the coefficients of Landau expansion of some ferroelectric liquid crystals[†]

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Abstract. The electroclinic effect in the smectic A phase of ferroelectric liquid crystals is a sensitive probe for measuring the soft mode response near the A–C* transition point. It is possible to evaluate several coefficients of the Landau theory describing the A–C* transition by simultaneously measuring the frequency dependence of both the optical signal and the current through the sample. We have made such measurements on a couple of homologous series [2S,3S]-4'-(2-chloro-3-methyl pentanoyloxy) phenyl-*trans*-4''-*n* alkoxy cinnamates synthesized in our laboratory. The results show that the Landau meanfield theory is adequate to describe the A–C* phase transition in these compounds.

Keywords. Electroclinic effect; ferroelectric liquid crystals; soft mode.

1. Introduction

The smectic C* liquid crystal is composed of chiral molecules. It consists of a stack of fluid layers in which the molecular long axes are tilted with respect to the layer normal. Meyer *et al* (1975) showed that the symmetry of such a medium allows it to be a ferroelectric. Consider a vertical cross section of a smectic C* layer passing through the layer normal Z and the director $\hat{n}$ (figure 1). The structure has a two-fold rotation axis about X . As the molecules are chiral, the YZ plane is not a mirror plane. The two-fold axis sustains the properties described by a polar vector along that axis. When the molecules have permanent transverse dipole moments, there can be a polarization P along the two-fold axis, i.e. the medium can become ferroelectric. The polarization is normal to the plane containing the director and the layer normal and hence such a ferroelectric is called transverse ferroelectric.

Many compounds exhibit a second order smectic C* to smectic A transition. In the latter, the molecules are upright and because of the rotational symmetry about the layer normal, it is not a ferroelectric liquid crystal. However, as was shown by Garoff and Meyer (1977, 1979), an electric field applied in the plane of the layers can produce a tilt of the molecules in the orthogonal plane of such a smectic A liquid crystal. This is known as the electroclinic effect. The electric field E couples to the transverse component of the molecular permanent electric dipole (p). This biases the free rotation of the molecules about their long axes since p tends to be parallel to the applied field. The system has a two-fold axis along the electric field. The plane containing the layer normal and p is a mirror plane in a non-chiral system. In the chiral system this mirror plane is lost. A molecular tilt with respect

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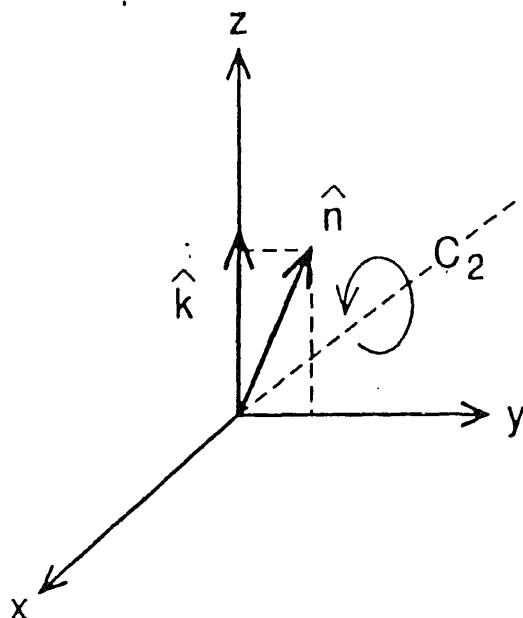


Figure 1. The C_2 symmetry operation in a ferroelectric smectic layer.

to the layer normal can then be induced in the orthogonal plane. This tilt is a linear function of the field (for small fields). A change in the director orientation produces a change in the direction of the optic axis, which gives rise to a linear electrooptic response. The electroclinic effect resembles piezo electricity in crystalline phases in some respects. However the fluid nature of the liquid crystalline phase does not allow any static shear strains which are associated with piezoelectricity in solid crystals. In the lowest order, the mean field expression for the free energy density of a smectic A liquid crystal made up of chiral molecules is given by (Garoff and Meyer 1979)

$$F = F_0 + \frac{1}{2} A(T) \theta^2 + \frac{1}{2} \chi_p^{-1} P^2 - PE - \frac{\epsilon_\infty E^2}{2} - cP\theta, \quad (1)$$

where F_0 is the ground state free energy of the smectic A phase, $A(T)$ the temperature dependent Landau coefficient given by $a(T - T_c)$, θ the induced tilt angle, χ_p the generalized susceptibility, P the induced polarization, E the external field, c the electroclinic coupling constant and ϵ_∞ the high frequency dielectric constant. Minimizing the free energy with respect to θ and P , we get

$$\theta = \frac{\chi_p c E}{A(T^*)}, \quad (2)$$

and

$$P = \chi_p E + \frac{\chi_p^2 c^2}{A(T^*)} E, \quad (3)$$

$$A(T^*) = a(T - T_c^*),$$

$$T_c^* = T_c + \frac{\chi_p c^2}{a}. \quad (4)$$

Due to the linear coupling $cP\theta$, the transition temperature is displaced in a chiral compound compared to its non-chiral analogue. When a sinusoidal field $Ee^{i\omega t}$ is applied to the cell, $A(T^*)$ is to be replaced by $[A(T^*)] + i\omega\eta$ where η is the soft-mode viscosity. Then we can expect the frequency dependences of the electroclinic tilt and of the electroclinic contribution to P to be Lorentzians with a relaxation frequency proportional to $[\tilde{a}((T - T_c^*)/T_c^*)]$, where

$$\tilde{a} = aT_c^*. \quad (5)$$

The phenomenological equation of motion can be written as

$$\eta(i\omega\theta) + \tilde{a} \left(\frac{T - T_c^*}{T_c^*} \right) \theta = c\chi_p E, \quad (6)$$

i.e.

$$\theta = \frac{c\chi_p E}{\tilde{a} \left(\frac{T - T_c^*}{T_c^*} \right) (1 + i\omega\tau)}, \quad (7)$$

where

$$\tau = \frac{\eta}{\tilde{a} \left(\frac{T - T_c^*}{T_c^*} \right)}, \quad (8)$$

is the relaxation time of the fluctuations of the order parameter θ . These equations can be rewritten in forms which will be useful to estimate the coefficients of the Landau expression following the procedure of Dupont *et al* (1991). Using (7), the RMS value of θ can be written as

$$|\theta| = \frac{c\chi_p E}{\tilde{a} \left(\frac{T - T_c^*}{T_c^*} \right) \sqrt{1 + \omega^2 \tau^2}}. \quad (9)$$

When the frequency is very low such that $\omega\tau \ll 1$,

$$e = \frac{\theta}{E} \approx \frac{c\chi_p}{\tilde{a} \left(\frac{T - T_c^*}{T_c^*} \right)}, \quad (10)$$

and using (3),

$$P = E \left[\chi_p + \frac{c^2 \chi_p^2}{\tilde{a} \left(\frac{T - T_c^*}{T_c^*} \right)} \right] \quad (9)$$

The dielectric permittivity of the medium along a direction perpendicular to director is then given by

$$\epsilon_{\perp} = (\epsilon_o + \chi_p) + \frac{c^2 \chi_p^2}{\tilde{a} \left(\frac{T - T_c^*}{T_c^*} \right)} \quad (10)$$

In the above equation, we have also to add the contribution from the very high frequency dielectric constant which arises from the polarizability due to the electron cloud. This contribution $\approx \epsilon_o \chi_{\infty}$ where $\chi_{\infty} = n_o^2$. Here n_o is the ordinary refractive index.

Using (10) and (12), by plotting $\epsilon_{\perp}$ vs e , the Y intercept yields $(\epsilon_o + \epsilon_o \chi_{\infty} + \chi_p)$ and the slope gives $c\chi_p$.

2. Experimental results and discussion

A block diagram of the experimental arrangement is shown in figure 2. Two conductive indium tin oxide coated glass plates are treated with polyimide and unidirectionally rubbed. A cell with a typical thickness of 7 to 10 μ is made using these plates. It is filled with the ferroelectric sample in the isotropic phase and mounted in a cell holder, placed in an INSTEC HSI-i microscope hot stage. The

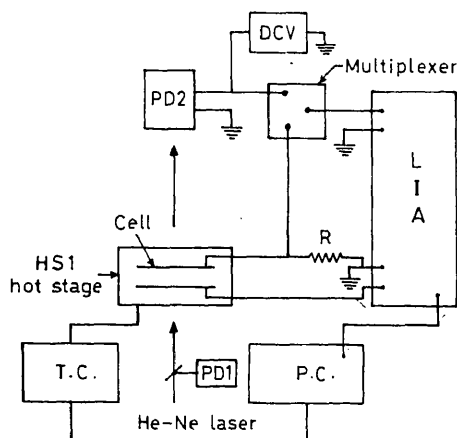


Figure 2. Block diagram of the experimental set-up used to measure the current electrooptic response.

temperature of the cell is regulated with the help of a PC. The temperature stability is around 10 mK. A standard resistance $R = 10$ ohms is connected in series with the cell to monitor the current through the cell. A He-Ne laser is used as the light source. Using a glass plate as a partial reflector, the laser intensity is monitored using a photodiode (OSI-5K). The intensity of light transmitted through the cell is measured using a PIN photodiode (Hamamatsu 1722) which has a response time of 5 ns. The output of the photodiode is connected to a preamplifier which is built around the fast operational amplifier BB3551. The preamplified output is fed to a lock-in-amplifier (PAR 5301) for optical signal measurement at the frequency of the applied field, and also to a DC multimeter (HP3457 A) to measure the DC part of the signal. We used a relay operated multiplexer as a switching device between the optical and conductivity signals. Suitable programmes were used to measure both the signals under identical conditions of frequency, applied voltage and temperature of the sample (spectrum interface).

We conducted measurements on two compounds of the homologous series [2*S*,3*S*]-4'-(2-chloro-3-methylpentanoyloxy) phenyl *trans*-4''-*n*-alkoxycinnamates synthesized in our chemistry laboratory (Shivkumar *et al* 1991). The general structural formula is shown in figure 3 and the transition temperatures are given in table 1.

The samples had some ionic impurities, which make a considerable contribution to the conductivity signal at low frequencies. But at higher frequencies ($\sim$ KHz) ions cannot follow the field and the contribution due to the capacitive coupling becomes prominent. This allows us to measure the electroclinic contribution to the dielectric constant which is needed in the analysis.

We have measured the frequency dependence of the electroclinic f signal starting from a few degrees above the A-C* transition temperature up to T_{AC} , for D9 and D10. The data was fitted to a Lorentzian $\theta(\omega)$ (see (9)) using a nonlinear least squares fitting programme. The calculated variations are shown as lines in figure 4 for D9. The relaxation frequency τ^{-1} was obtained as a function of temperature using this procedure (figure 5). It shows that the relaxation frequency increases linearly with temperature in accordance with the prediction of the Landau theory (see (8)). The electroclinic contribution to the dielectric constant relaxes beyond that frequency. Similar measurements were made on D10 also. Figure 6 shows the τ^{-1} variation with temperature for D10.

The typical frequency dependence of the current (which is essentially capacitive)

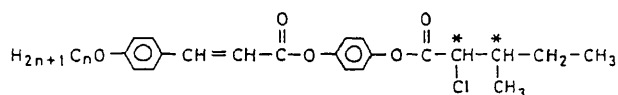


Figure 3. The general structural formula of [2*S*,3*S*]-4'-(2-chloro-3-methyl pentanoyloxy) phenyl-*trans*-4''-*n*-alkoxy cinnamates used in our experiments.

Table 1. The transition temperatures (in $^{\circ}\text{C}$) of [2*S*,3*S*]-4'-(2-chloro-3-methyl-pentanoyloxy)phenyl *trans*-4''-*n*-alkoxycinnamates.

Compound	<i>n</i>	C	S_C^*	S_A	N^*	<i>I</i>
D9	9	.	69.0	.	78.0	95.0
D10	10	.	56.0	.	80.0	98.5
						97.0
						99.0

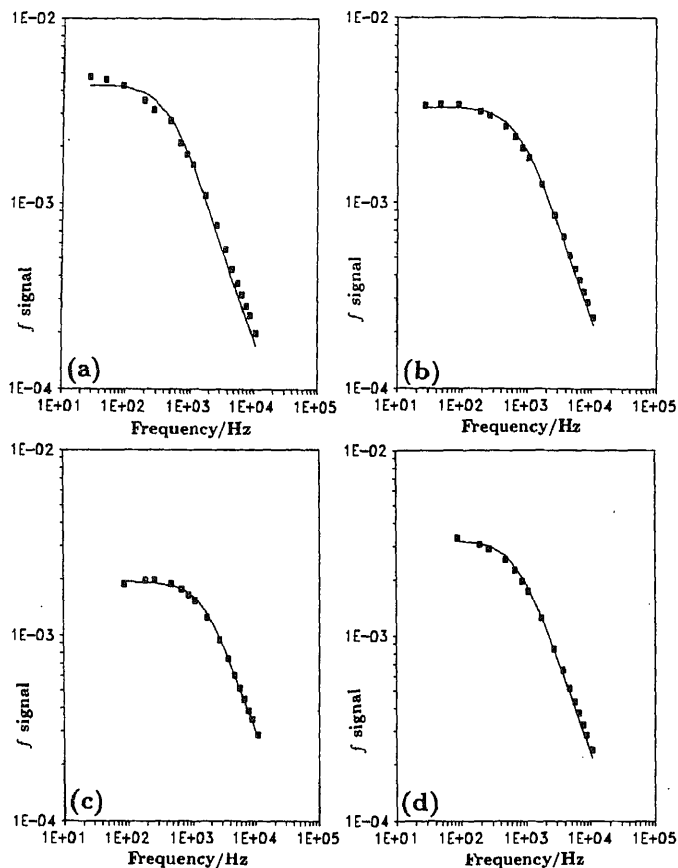


Figure 4. Variation of f signal as a function of frequency for the compound D9 at (a) 339.3 K, (b) 339.5 K, (c) 339.7 K and (d) 340.1 K. Solid lines show the fitted Lorentzians.

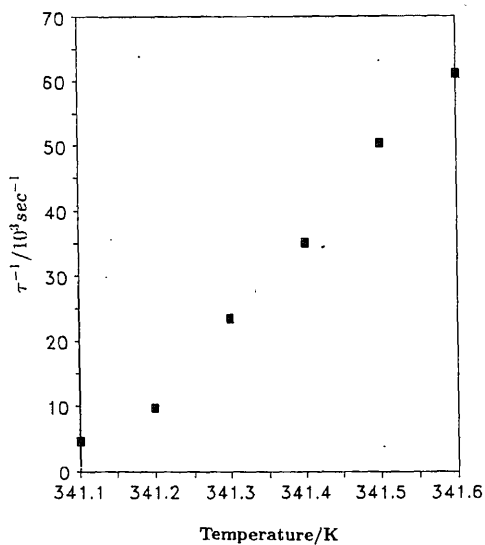


Figure 5. Variation of τ^{-1} as a function of temperature for D9.

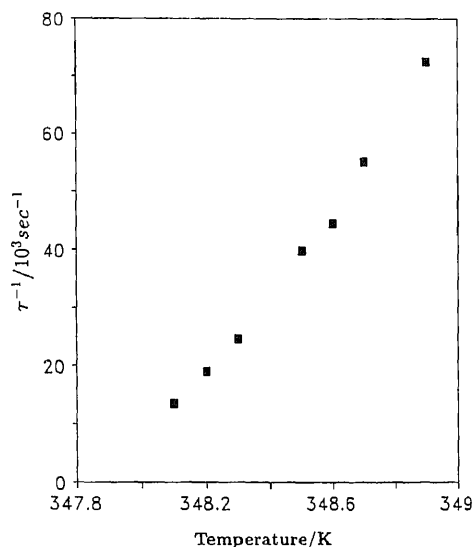


Figure 6. Variation of τ^{-1} as a function of temperature for D10.

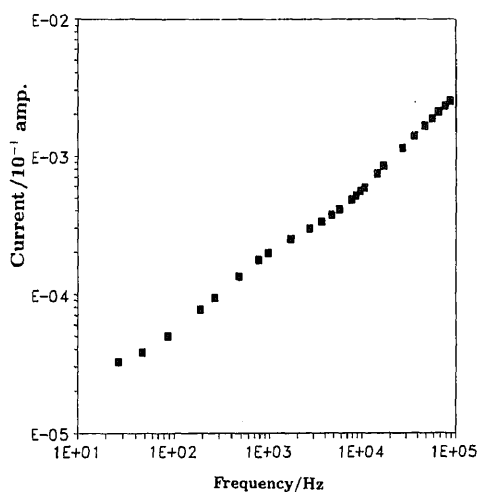


Figure 7. Variation of current as a function of frequency for the compound D9 at 342 K.

is shown in figure 7. It shows that there is a change of slope when the electroclinic contribution to the current relaxes.

For D9 and D10, we have made measurements of the current as a function of temperature at 1960 and 5700 Hz respectively, simultaneously with the measurement of the optical signal. We use the data in a temperature range in which these frequencies are below the relaxation frequency and use (10–12) in further analysis of the data.

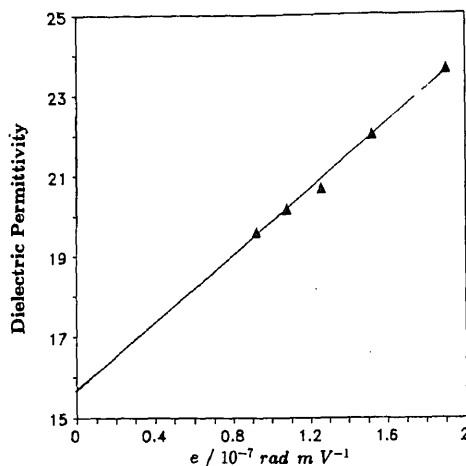


Figure 8. Dielectric permittivity as a function of the EC coefficient for the compound D9.

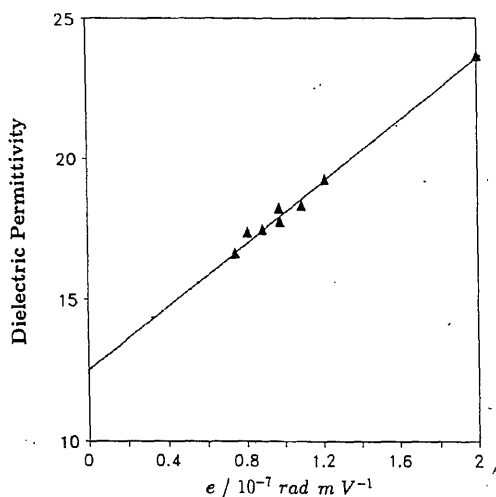


Figure 9. Dielectric permittivity as a function of the EC coefficient for the compound D10.

The capacitance of the cell is given by

$$C = \left| \frac{I}{\omega V} \right| = \epsilon_{\perp} C_0 + C_{\text{spacer}}, \quad (13)$$

where $\epsilon_{\perp}$ is the dielectric permittivity of the medium along a direction perpendicular to the director, C_0 the capacitance of the part of the empty cell without the spacer which was calculated by the geometrical parameters of the cell, C_{spacer} is the capacitance of the part of the cell which had mylar spaces which was also calculated

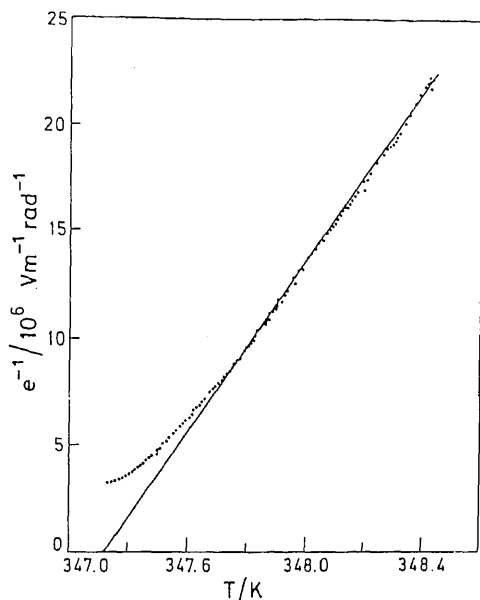


Figure 10. Temperature dependence of the inverse electroclinic coefficient, e^{-1} of D9 at 1960 Hz.

by the geometrical parameters. The above equation can be rewritten as

$$\frac{C}{C_0} = \frac{C_{\text{spacer}}}{C_0} + \epsilon_{\perp}, \quad (14)$$

from which $\epsilon_{\perp}$ was evaluated. We plotted $\epsilon_{\perp}/\epsilon_0$ vs $e = (\theta/E)$ at various temperatures. Figure 8 shows the variation for D9 and figure 9 for D10.

As expected from (10) to (12) the variation of $\epsilon_{\perp}$ vs e is a straight line within the accuracy of our measurements. As discussed after (12) the Y-intercept yields $[1 + \chi_{\infty} + (\chi_p/\epsilon_0)]$ and the slope gives $c\chi_p$. Here $\chi_{\infty} = n_o^2$, where n_o is the ordinary index ≈ 1.6 . Hence from the Y intercept we can calculate χ_p and using this value the coupling coefficient c can be calculated from the slope. From the graph of e^{-1} vs T , using (10), the corresponding slope gives $\tilde{a}$. In the case of D9 and D10, from figures 10 and 11 the slopes have the magnitudes 2.1×10^7 and 1.6×10^7 respectively. Using (8), by substituting the value of $\tilde{a}$, the viscosity coefficient η can be calculated. We have shown the calculated values of the various quantities in table 2.

The values given in table 2 are broadly in the expected range, and comparable to those given by Dupont *et al* (1991) for other compounds. Our values of χ_p/ϵ_0 for D9 and D10 are somewhat larger than the values obtained by Dupont *et al* (1991) for their compounds. This may partly be due to the presence of an additional COO group in the molecular structure of the compounds that we have used. This will enhance the lateral dipole moment of the molecule. The viscosity coefficient η is 0.01 Ns/m^2 which is of the right order for liquid crystals at high temperatures. These numbers are also consistent with the fitting parameters obtained on another compound D8 which belong to the same homologous series (Padmini

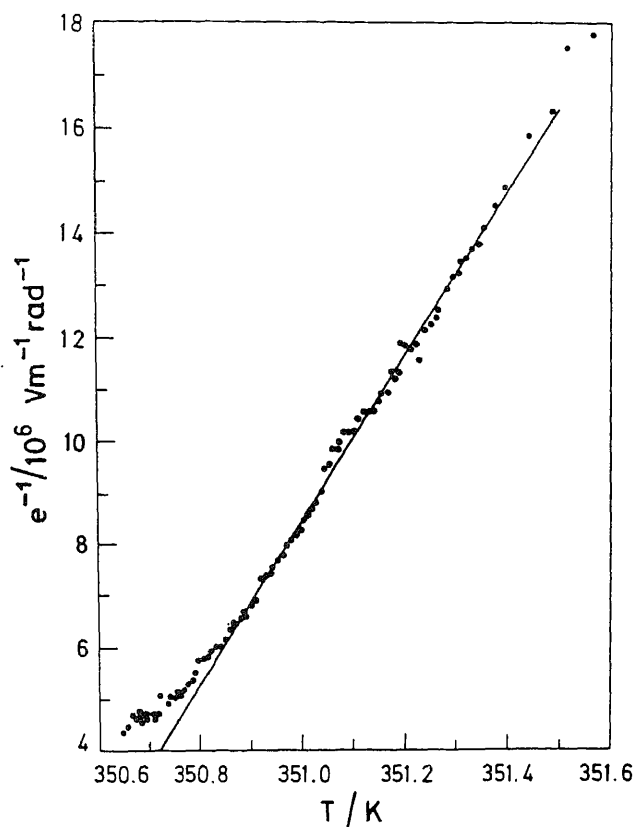


Figure 11. Temperature dependence of the inverse electroclinic coefficient, e^{-1} of D10 at 1960 Hz.

Table 2. Coefficients of the Landau theory.

Coefficients	Compound	
	D9	D10
χ_p / ϵ_0	11.6	8.5
$\chi_p (\text{cm}^{-2} \text{rad}^{-1})$	3.73×10^{-4}	4.87×10^{-4}
$c (\text{NC}^{-1} \text{rad}^{-1})$	0.36×10^7	0.65×10^7
$a (\text{Nm}^{-2} \times \text{K}^{-1})$	0.78×10^4	0.78×10^4
$\Delta T_c (\text{K})$	1.7	0.4
$\eta (\text{N sm}^{-2})$	0.01	0.01

et al 1993) where we analyzed only the optical data in terms of the Garoff-Meyer model. However, we should note that in the present analysis η is assumed to be temperature independent.

Thus the dynamic measurements on the soft mode electroclinic effect in the A* phase can be used to estimate all the parameters of the linearized Landau model of the A-C* transition.

Acknowledgement

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An electron spin resonance study of Mn^{2+} doped calcium hydrazine carboxylate monohydrate

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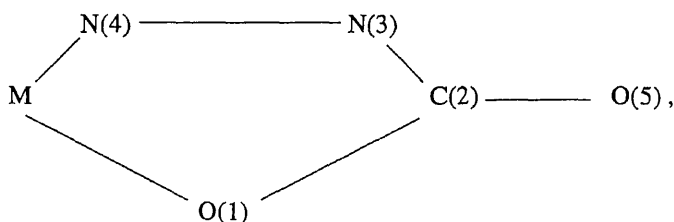
Abstract. Single crystals of calcium hydrazine carboxylate, monohydrate have been studied by ESR of Mn^{2+} doped in the calcium sites. X-band ESR indicated a large crystal field splitting necessitating experiments at Q band. The analysis shows two magnetically inequivalent (but chemically equivalent) sites with $g_{xx} = 2.0042 \pm 0.0038$, $g_{yy} = 2.0076 \pm 0.0029$, $g_{zz} = 2.0314 \pm 0.001$, $A_{zz} = 0.0099 \pm 0.0002 \text{ cm}^{-1}$, $A_{xx} = 0.0092 \pm 0.0002 \text{ cm}^{-1}$, $A_{yy} = 0.0082 \pm 0.0002 \text{ cm}^{-1}$, $D = 3/2 D_{zz} = 0.0558 \pm 0.0006 \text{ cm}^{-1}$, and $E = 1/2 (D_{xx} - D_{yy}) = 0.0127 \pm 0.0002 \text{ cm}^{-1}$.

One of the principal components of the crystal field, (D_{zz}) , is found to be along the $Ca \leftrightarrow Ca$ direction in the structure and a second one, (D_{xx}) , along the perpendicular to the plane of the triangle formed by three neighbouring calciums. The A tensor is found to have an orientation different from that of the g and D tensors reflecting the low symmetry of the Ca^{2+} sites.

Keywords. Electron spin resonance; Mn^{2+} ESR; low symmetry effects in ESR; $Ca(N_2H_3COO)_2 \cdot H_2O$.

1. Introduction

The hydrazine carboxylate compounds consisting of the complexes of 3d-metals, calcium and magnesium with hydrazine carboxylic acid have attracted recent scientific attention (Ravindranathan and Patil 1985). While they present various types of octahedral coordination, all of them contain pentatomic chelate rings of the type



which are similar to rings formed by α -amino acids with the same metals (Freeman 1967). Therefore, these complexes can serve as model compounds for non-crystallizable compounds of α -amino acids. Braibanti *et al* (1971) determined the crystal structure of calcium hydrazine carboxylate monohydrate, $Ca(N_2H_3COO)_2 \cdot H_2O$ and found that it belongs to the triclinic system with $Z = 2$. The two calcium ions were surrounded by six oxygens and two nitrogens forming what can be roughly

described as a pentagonal bipyramid, with a centred phase analogous to that observed in CaCl_2 glycyglycylglycine $\cdot 3\text{H}_2\text{O}$. We are reporting here the results of our detailed single crystal ESR studies of the compound in X- and Q-bands, of Mn^{2+} doped dilutely in place of the Ca^{2+} ions. It was also interesting to characterize the ESR of Mn^{2+} in this not so common low symmetry surrounding.

2. Experimental

Single crystals of Mn^{2+} doped calcium hydrazine carboxylate monohydrate (CHCM) were prepared by the following procedure.

An aqueous solution containing Ca^{2+} ions was treated with hydrazine hydrate (99%) saturated with $\text{CO}_2(\text{g})$. The resulting mixture was allowed to stand exposed to the atmosphere. A colourless solid separated from the solution in about 8–10 days. The crystals were washed with alcohol and stored over P_2O_5 in a vacuum desiccator. The composition of the crystals was checked by conventional chemical analysis to be $\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. Calcium content was fixed by EDTA titration and hydrazine was estimated by titration against standard KIO_3 solution under Andrews conditions. The water content was determined by the weight loss.

Manganese (Mn^{2+}) doped $\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ was prepared by treating an aqueous solution containing Ca^{2+} and Mn^{2+} ions in required concentrations with the ligand $\text{N}_2\text{H}_3\text{COO}^-$ as above. The product, $\text{Ca}_{1-x}\text{Mn}_x(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ crystallized from the mixture. The crystals were pale pink in colour indicating the presence of Mn^{2+} in $\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. Doping of Mn^{2+} in $\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ is possible due to the isomorphic crystal structures of $\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and $\text{Mn}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and comparable ionic sizes of Ca^{2+} (0.99 Å) and Mn^{2+} (0.8 Å).

The ESR studies of the single crystals of the compound were carried out at X-band using a Varian E-109 spectrometer and at Q-band using a E-112 X/Q-band spectrometer. A 100 kHz magnetic field modulation was used. Spectra were recorded for different orientations of the magnetic field in three mutually orthogonal planes. A small amount of DPPH was used as the *g*-marker.

3. Results and analysis

Some typical spectra at X-band ($\nu = 9.15$ GHz) are shown in figure 1. In general, the ESR spectra of Mn^{2+} ($S = 5/2$, $I = 5/2$) consist of five fine-structure multiplets, each consisting of a six-line hyperfine structure. It is apparent from the figure that the Mn^{2+} is experiencing a large crystal field splitting. Therefore, a treatment involving the zero field splitting as a perturbation on the Zeeman interaction is not valid at X-band. So experiments were repeated at Q-band ($\nu = 35.45$ GHz). Figure 2 shows some spectra at Q-band for CHCM at room temperature along with the assignment of the rotation axes with respect to the crystal morphology. Since the crystal belongs to the triclinic system, the crystallographic axes are not orthogonal to each other. Since $Z = 2$ (Braibanti *et al* 1971), the observed spectrum is a superposition of two 30-line spectra. The unit cell of CHCM is triclinic and no apparent symmetry operation relates the two Ca^{2+} sites. Therefore the two Mn^{2+} sites can, in principle, be chemically as well as magnetically inequivalent.

Since the system is of low symmetry and therefore, in general no principal axis

of any tensor is expected to be along any of the crystallographic axes it was necessary to carry out angular variation experiments in three orthogonal planes. Moreover, in such a situation it is possible that the principal axes systems of the

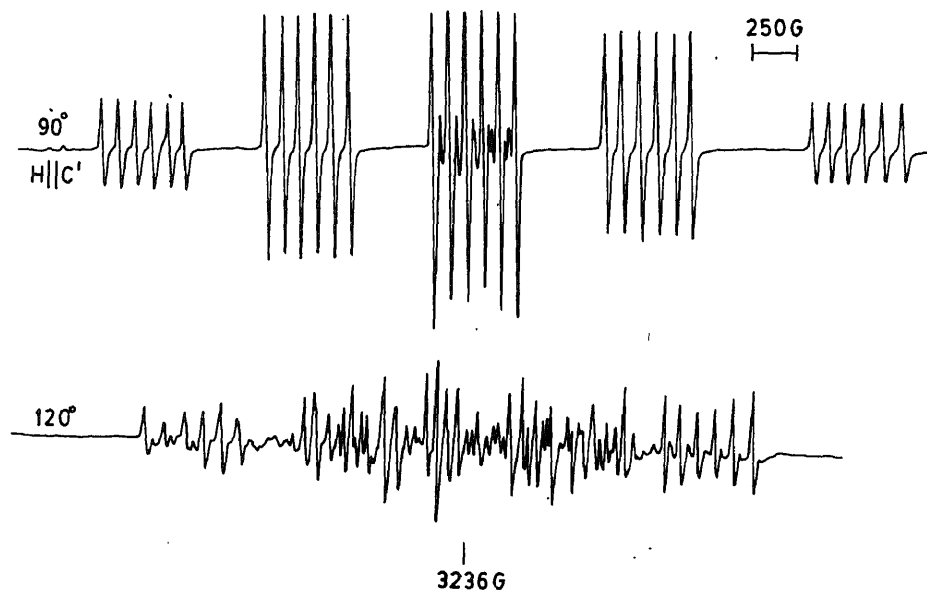


Figure 1. Some typical spectra at X-band ($\nu = 9.15$ GHz) of Mn^{2+} doped calcium hydrazine carboxylate monohydrate.

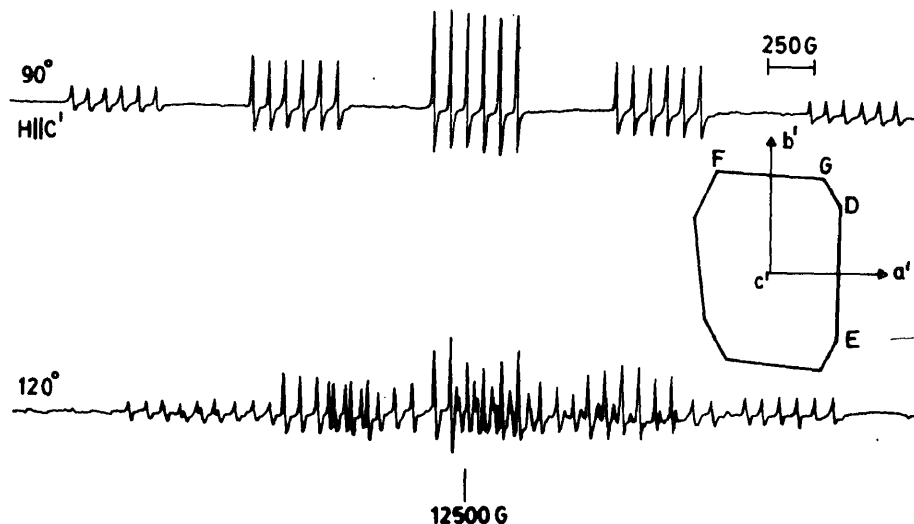


Figure 2. Some typical spectra at Q-band ($\nu = 35.45$ GHz) of Mn^{2+} doped calcium hydrazine carboxylate monohydrate. (The orientation of the axes of rotation with respect to the crystal morphology is also indicated).

three tensors $\mathbf{g}$, $\mathbf{A}$ and $\mathbf{D}$ in the spin Hamiltonian are not coincident with each other (Pilbrow and Lowrey 1971). For the analysis of such a case the method due to Lund and Vanngard (1965) which is a generalization to hyperfine and crystal field interactions, of the Schonland (1959) method of the analysis of Zeeman interaction seems to be most suitable. It enables the determination of the magnitudes and orientations of the three tensors through experiments involving the rotation of the magnetic field in three orthogonal planes of the crystal. Therefore, we have used this method for the analysis and a brief description of the same follows.

We start with the spin Hamiltonian

$$\mathcal{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathcal{H}_a, \quad (1)$$

where

$$\mathcal{H}_a = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}, \quad (2)$$

with the conventional meanings for the symbols. The first term on the right hand side of (1) represents the Zeeman interaction and $\mathcal{H}_a$ stands for the crystal field and the hyperfine interactions. For the Q-band spectra, since the Zeeman interaction is of much larger strength, one can safely treat the crystal field and the hyperfine interactions as perturbations. Then, the energy of the system, correct up to the second order terms in perturbation can be written as

$$W(M_z) = \beta g H M_z + \langle M_z | H_a | M_z \rangle + \sum_{M_z' \neq M_z} \frac{|\langle M_z | H_a | M_z' \rangle|^2}{\beta g H (M_z - M_z')}. \quad (3)$$

In order to extract $\langle M_z | \mathcal{H}_a | M_z \rangle$ from the experimental data one must first eliminate the contribution from the off-diagonal terms. If one reverses the signs of M_z and M_z' in (3) it is found that

$$W(-M_z) = -\beta g H M_z + \langle M_z | H_a | M_z \rangle - \sum_{M_z' \neq M_z} \frac{|\langle M_z | H_a | M_z' \rangle|^2}{\beta g H (M_z - M_z')}, \quad (4)$$

and hence the sum $W(M_z) + W(-M_z)$ is independent of the off-diagonal terms. In practice, since H is varied while ν is kept constant, this elimination of the off-diagonal terms is accomplished by subtracting from each other, equations corresponding to transitions with electronic and nuclear magnetic quantum numbers of opposite signs, such as $(M_z, M_I \longleftrightarrow M_z - 1, M_I)$ and $(-M_z + 1, -M_I \longleftrightarrow -M_z, -M_I)$. To facilitate the evaluation of the eigenvalues of the spin Hamiltonian (1) a new coordinate system with $\mathbf{H} \cdot \mathbf{g}$ as the axis of quantization (Z axis) is chosen. In this coordinate system one can explicitly write the perturbing Hamiltonian $\mathcal{H}_a$ in the form

$$\mathcal{H}_a = \frac{\mathbf{H} \cdot \mathbf{g} \cdot \mathbf{D} \cdot \mathbf{g} \cdot \mathbf{H}}{|\mathbf{H} \cdot \mathbf{g}|^2} (3S_z^2 - S^2) + \frac{\mathbf{H} \cdot \mathbf{g} \cdot \mathbf{A}}{|\mathbf{H} \cdot \mathbf{g}|} S_z I_z. \quad (5)$$

Then, the energy for the transition ($M_z, M_I \longleftrightarrow M_z - 1, M_I$) is given, to the first order in perturbation, by

$$E = W(M_z, M_I) - W(M_z - 1, M_I) = \beta gH + F(M_z - 1/2) + KM_I, \quad (6)$$

where
$$F = \frac{\mathbf{H} \cdot \mathbf{g} \cdot \mathbf{D} \cdot \mathbf{g} \cdot \mathbf{H} \times 3}{|\mathbf{H} \cdot \mathbf{g}|^2}$$

and
$$K = \frac{|\mathbf{H} \cdot \mathbf{g} \cdot \mathbf{A}|}{|\mathbf{H} \cdot \mathbf{g}|}. \quad (7)$$

Taking the magnetic field H along the unit vector $\mathbf{l}$ we get

$$F \mathbf{g}^2/3 = \mathbf{l} \cdot \mathbf{T}^{(f)} \cdot \mathbf{l},$$

where $\mathbf{T}^{(f)} = \mathbf{g} \cdot \mathbf{D} \cdot \mathbf{g},$

and $K^2 \mathbf{g}^2 = \mathbf{l} \cdot \mathbf{T}^{(h)} \cdot \mathbf{l},$

and $\mathbf{g}^2 = \mathbf{l} \cdot \mathbf{T}^{(g)} \cdot \mathbf{l},$

where $\mathbf{T}^{(g)} = \mathbf{g}^2. \quad (8)$

Thus effecting the elimination of the contributions from second order terms one can calculate $\mathbf{g}^2$, $F\mathbf{g}^2/3$, and $K^2\mathbf{g}^2$. These quantities can be fitted to the Schonland form

$$\alpha' + \beta' \cos 2\theta + \gamma' \sin 2\theta, \quad (9)$$

where α' , β' and γ' are constants. From these constants the components of the tensors $\mathbf{T}^{(g)}$, $\mathbf{T}^{(f)}$ and $\mathbf{T}^{(h)}$ can be calculated. Figure 3 shows the experimental points of four transitions $M_z, M_I \longleftrightarrow M_z - 1, M_I$ where $M_z = 5/2, 3/2, M_I = 5/2$ and $M_z = -5/2, -3/2, M_I = -5/2$, at Q-band, fitted to the spin Hamiltonian in (1) in the three orthogonal planes. Figure 4 shows the fit at X-band in a 'c' plane for the same transitions. It can be seen that the fit between the experimental points and the calculated points at X-band is poor, while for Q-band the fit is very good. The matrix $\mathbf{T}^{(g)}$ formed from the constants α' , β' and γ' (9) in the three planes at Q-band were diagonalized to yield the principal components of the g tensor and the direction cosines with respect to the rotation axes 1, 2 and 3. The crystal field and the hyperfine coupling tensors were calculated from the matrices formed from the fits corresponding to $F\mathbf{g}^2/3$ and $K^2\mathbf{g}^2$ respectively, to be

$$\mathbf{D} = \mathbf{g}^{-1} \cdot \mathbf{T}^{(f)} \cdot \mathbf{g}^{-1},$$

and

$$\mathbf{A}^2 = \mathbf{g}^{-1} \cdot \mathbf{T}^{(h)} \cdot \mathbf{g}^{-1}. \quad (10)$$

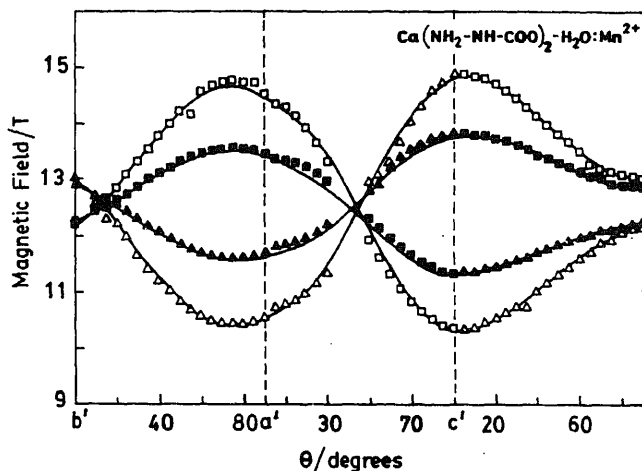


Figure 3. Fitting curves of the experimental points corresponding to the four transitions $M_z, M_I \leftrightarrow M_z - 1, M_I$ [$M_z = 5/2, 3/2; M_I = 5/2$ and $M_z = -1/2, -3/2; M_I = -5/2$] at Q-band to the spin Hamiltonian in (1).

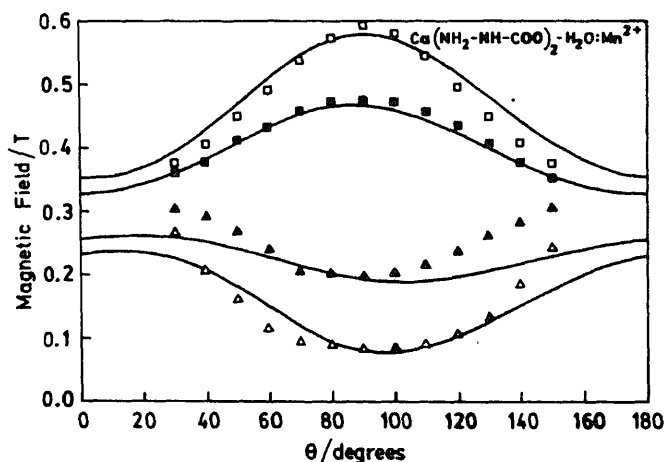


Figure 4. Fitting curves of the experimental points corresponding to the four transitions $M_z, M_I \leftrightarrow M_z - 1, M_I$ [$M_z = 5/2, 3/2; M_I = 5/2$ and $M_z = -(1/2), -(3/2); M_I = -(5/2)$] in the $a'b'$ plane at X-band to the spin Hamiltonian in (1).

The matrices $\mathbf{D}$ and $\mathbf{A}^2$ were diagonalized to yield the principal components along with the direction cosines. Table 1 summarizes these results for one of the sites and table 2 for the other site.

As a check on the spin Hamiltonian parameters obtained in this way, we have also attempted to calculate the line positions using the parameters and compare them with the corresponding experimental values. Now we describe briefly, the procedure adopted to do the same using the values of tables 1 and 2 for the spin Hamiltonian parameters of (1). The field values for the centres of the hyperfine

Table 1. Principal components of $\mathbf{g}$, $\mathbf{D}$ and $\mathbf{A}$ tensors along with the direction cosines for site 1, with respect to the laboratory frame a' , b' , c' for Mn^{2+} in CHCM.

Principal components		Direction cosines		
		a'	b'	c'
g_{zz}	$2.0274 \pm 8.79 \times 10^{-4}$	$0.9671 \pm 1.94 \times 10^{-4}$	$0.17443 \pm 5.23 \times 10^{-4}$	$0.1851 \pm 5.55 \times 10^{-4}$
g_{yy}	$2.0090 \pm 8.34 \times 10^{-4}$	$-0.2002 \pm 5.79 \times 10^{-4}$	$0.9709 \pm 4.73 \times 10^{-4}$	$-0.1310 \pm 3.106 \times 10^{-3}$
g_{xx}	$2.0004 \pm 8.36 \times 10^{-4}$	$0.1568 \pm 1.052 \times 10^{-3}$	$0.1638 \pm 2.976 \times 10^{-3}$	$0.9740 \pm 3.385 \times 10^{-4}$
D_{zz}/G	390.2 ± 4.3	$0.9656 \pm 0.3 \times 10^{-4}$	$-0.2585 \pm 1.1 \times 10^{-4}$	$0.0264 \pm 0.46 \times 10^{-4}$
D_{yy}/G	-55.9 ± 4.7	$0.2565 \pm 1.03 \times 10^{-4}$	$0.9645 \pm 0.32 \times 10^{-4}$	$-0.0621 \pm 1.72 \times 10^{-4}$
D_{xx}/G	-341.9 ± 5.7	$0.0416 \pm 0.67 \times 10^{-4}$	$0.0532 \pm 1.65 \times 10^{-4}$	$-0.9977 \pm 0.1 \times 10^{-4}$
A_{zz}/G	106.8 ± 1.6	0.7343 ± 0.0108	-0.4709 ± 0.0557	0.4856 ± 0.0381
A_{yy}/G	80.2 ± 3.1	$0.6670 \pm 0.16 \times 10^{-4}$	0.3814 ± 0.0109	$0.6399 \pm 0.48 \times 10^{-4}$
A_{xx}/G	102.2 ± 2.1	0.1161 ± 0.0577	0.7937 ± 0.0279	-0.5789 ± 0.0507

Table 2. Principal components of $\mathbf{g}$, $\mathbf{D}$ and $\mathbf{A}$ tensors along with the direction cosines for site 2, with respect to the laboratory frame a' , b' , c' for Mn^{2+} in CHCM.

Principal components		Direction cosines		
		a'	b'	c'
g_{zz}	$2.0314 \pm 1.01 \times 10^{-3}$	$0.20408 \pm 0.0103 \times 10^{-4}$	$0.97778 \pm 2.24 \times 10^{-3}$	$-0.04634 \pm 1.4 \times 10^{-3}$
g_{yy}	$2.0077 \pm 2.93 \times 10^{-3}$	$0.9697 \pm 2.17 \times 10^{-3}$	$0.19543 \pm 1.01 \times 10^{-3}$	$0.14646 \pm 7.18 \times 10^{-3}$
g_{xx}	$2.0043 \pm 0.38 \times 10^{-4}$	$-0.1341 \pm 7.16 \times 10^{-3}$	$0.07482 \pm 3.12 \times 10^{-3}$	$0.98811 \pm 1.09 \times 10^{-3}$
D_{zz}/G	-393.6 ± 4.6	$0.1794 \pm 8.8 \times 10^{-4}$	$0.9837 \pm 1.62 \times 10^{-4}$	$0.0139 \pm 5.97 \times 10^{-4}$
D_{yy}/G	76.7 ± 2.0	$0.9834 \pm 1.54 \times 10^{-4}$	$0.1789 \pm 8.93 \times 10^{-4}$	$-0.0315 \pm 2.45 \times 10^{-4}$
D_{xx}/G	345.0 ± 4.3	$0.02845 \pm 2.57 \times 10^{-4}$	$0.0194 \pm 0.24 \times 10^{-4}$	$0.9994 \pm 0.01 \times 10^{-4}$
A_{zz}/G	105.4 ± 2.2	$0.7775 \pm 5.815 \times 10^{-3}$	$0.4105 \pm 8.61 \times 10^{-4}$	$-0.4763 \pm 8.74 \times 10^{-3}$
A_{yy}/G	87.2 ± 2.8	$-0.2891 \pm 2.02 \times 10^{-3}$	$0.9061 \pm 5.2 \times 10^{-4}$	$0.3080 \pm 3.37 \times 10^{-3}$
A_{xx}/G	97.8 ± 2.5	$0.5584 \pm 7.04 \times 10^{-3}$	$-0.1025 \pm 7.91 \times 10^{-3}$	$0.8232 \pm 3.8 \times 10^{-3}$

sextets are calculated for the Q-band spectra corrected to the third order in perturbation. To accomplish this it is necessary to calculate the spectrum for a given orientation of the magnetic field in the laboratory frame from spin Hamiltonian parameters in the principal axes frame given in the tables. We have followed the procedure adopted by Okumura (1962) and Balasivasubramanian *et al* (1983) for this purpose.

The spin Hamiltonian expressed in terms of the polar coordinates of the crystal field system is given by (Okumara 1962),

$$\mathcal{H} = \beta g H S_z + a [(S_z^2 - 1)/3S(S+1)] + b (2S_z S_+ - S_+)$$

$$+ b^* (2S_z S_- + S_-) + C S_+^2 + C^* S_-^2 + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}, \quad (11)$$

where a , b and c are functions in the polar and azimuthal coordinates θ and ϕ of the magnetic field H with respect to the crystal field system. Table 1 provides the relation between the laboratory frame a' , b' , c' system of coordinates and the crystal field system of coordinates. Therefore to evaluate the polar and azimuthal angles θ and ϕ , it is necessary to transform the system of coordinates of the laboratory frame to the system of coordinates of the crystal field. From table 1, it can be seen that the principal component D_{xx} is parallel to the laboratory axis c' . Therefore by applying the Euler method of the rotation of the laboratory frame around the c' -axis by an angle α , say, (it is the same as the angle between D_{yy} and b' -axis), the system of coordinates a' , b' , c' will transform to the principal system of coordinates D_{xx} , D_{yy} , D_{zz} . The matrix of transformation is

$$R(\alpha) = \begin{vmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{vmatrix}. \quad (12)$$

The direction cosines of the magnetic field H in $c'a'$ plane with respect to the principal system of coordinates are given by

$$\begin{vmatrix} \cos \theta \\ -\sin \theta \sin \phi \\ \sin \theta \cos \phi \end{vmatrix} = \begin{vmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} \sin \theta' \\ 0 \\ \cos \theta' \end{vmatrix}, \quad (13)$$

where θ' is the angle between the magnetic field H and the c' axis in $c'a'$ plane. From (13), the values of the polar and the azimuthal angles θ and ϕ can be calculated. Using the angles θ and ϕ evaluated in this way, the positions of the centres of the fine structure multiplets corrected to third order in perturbation have been calculated (Balasivasubramanian *et al* 1983) as follows:

$$|\pm \frac{5}{2}\rangle \longleftrightarrow |\pm \frac{3}{2}\rangle:$$

$$h\nu = G + 4a + \frac{1}{G} [128 bb^* - 16 cc^*] \\ + \frac{1}{G^2} [\mp 576 abb^* \mp 24 acc^* \pm 480 (bbc^* + b^*b^*c)],$$

$$|\pm \frac{3}{2}\rangle \longleftrightarrow |\pm \frac{1}{2}\rangle:$$

$$h\nu = G \pm \frac{1}{2} a + \frac{1}{G} [-16 bb^* + 20 cc^*] \\ + \frac{1}{G^2} [\pm 192 abb^* \mp 132 acc^* \mp 480 (bbc^* + b^*b^*c)],$$

$$\text{and} \quad |+\frac{1}{2}\rangle \longleftrightarrow |-\frac{1}{2}\rangle:$$

$$h\nu = G + \frac{1}{G} [-64 bb^* + 32 cc^*].$$

Where

$$G = g \beta H,$$

$$a = [D(3 \cos^2 \theta - 1) + \frac{3}{2} \sin^2 \theta \cos 2\varphi],$$

$$b = [-D \sin \theta \cos \theta + \frac{1}{4} E \sin \theta (1 + \cos \theta) \exp(2i\varphi) - (1 - \cos \theta) \exp(2i\varphi)] \exp(-i\varphi),$$

$$c = [\frac{1}{4} D \sin^2 \theta + \frac{1}{8} E (1 + \cos \theta)^2 \exp(2i\varphi) + (1 - \cos \theta)^2 \exp(-2i\varphi)] \exp(-2i\varphi).$$

Figure 5 shows the plots of the calculated positions of the centres of the fine structure multiplets corrected to third order in perturbation and the experimental points in the $c'a'$ plane. From this figure it can be seen that the calculated line positions of the spectrum at high field side are quite satisfactory. However, at low field side there is a departure of the calculated points from the experimental ones. At this stage it must be noted that in these calculations we neglect the effect of the higher order correction in the hyperfine interaction. Also from tables 1 and 2 it is seen that the hyperfine tensor **A** is not coincident with **g** and **D** tensors. These facts, along with the anisotropy of the hyperfine interaction (tables 1 and 2) result in the departure in the calculation of the centres of the fine structure multiplets and thus cause a slight difference in the calculated and the experimental line positions.

4. Discussion

X-ray structure of calcium hydrazine carboxylate monohydrate shows that the

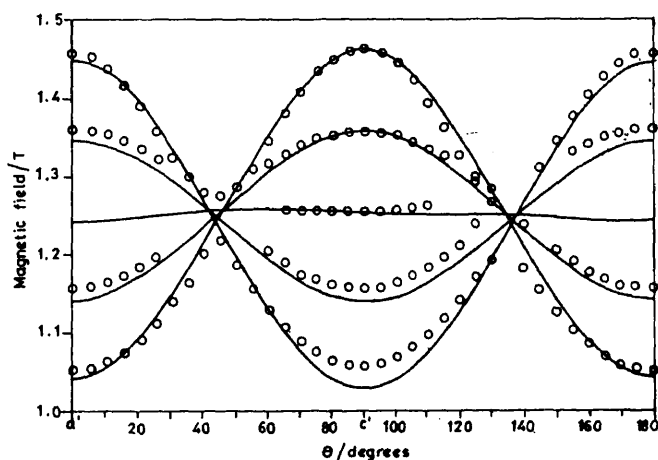


Figure 5. Calculated curves and experimental points of the centres of the fine structure multiplets for Q-band spectra in the $a'c'$ plane.

complex crystallizes in the triclinic space group $P1$ with two formula units per unit cell. The structure consists of chains parallel to $[001]$ formed by a sequence of cations and anions (figure 6). The resulting coordination number around the Ca^{2+} ions is 8 with six O atoms and two N atoms. Two O atoms are shared between two Ca^{2+} ions and form bridges along the c -direction with an angle of 145.03° inclined to each other while the three neighbouring Ca^{2+} ions form a triangle with an angle of about 115° between the $\text{Ca(I)} \rightarrow \text{Ca(II)}$ and the $\text{Ca(I)}\text{--Ca(III)}$ directions. The direction of the normal to the plane of the triangle is common to all the Ca-triangles in the structure and leads to the coincidence of the spectra for the two sites of the paramagnetic centres for the magnetic field along that direction. From tables 1 and 2, it can be seen that (i) the two sites show very similar magnitudes of the principal components of the three tensors $\mathbf{g}$, $\mathbf{D}$ and $\mathbf{A}$, thus showing that the two sites are only magnetically inequivalent, and (ii) the D_{xx} components of the two sites are very nearly coincident with each other and are

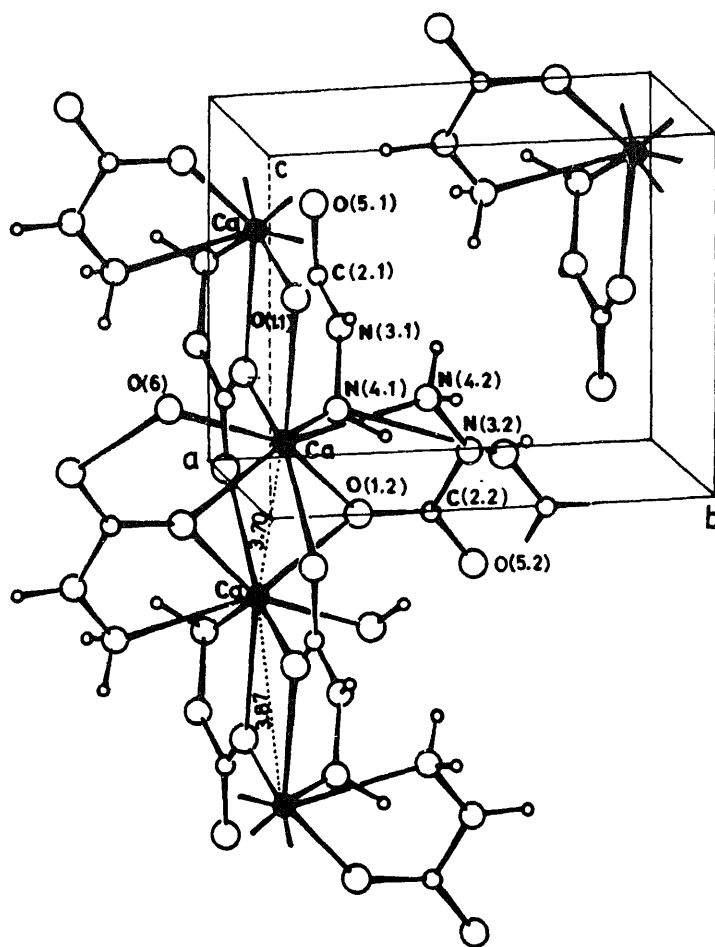


Figure 6. Structure of CHCM showing $\text{Ca} \leftrightarrow \text{O}$ bridges along the $[001]$ direction.

parallel to the c' direction, which is consistent with the fact that parallel to the c' direction one observes only one set of Mn^{2+} signals. Also from the tables it can be seen that the D_{zz} components of the two sites are inclined to each other at an angle of about 115° . Therefore, it can be concluded that the D_{zz} component of the crystal field tensor is parallel to the $Ca \longleftrightarrow Ca$ direction and the D_{xx} component [$D_{xx}(1)//D_{xx}(2)$] is along the normal to the plane of the triangles formed by the three neighbouring Ca^{2+} ions.

5. Conclusion

The ESR spectra of Mn^{2+} substituting dilutely for Ca^{2+} in calcium hydrazine carboxylate monohydrate single crystals show interesting low symmetry effects. The Mn^{2+} ions experience large crystal field interactions. The hyperfine tensor has a different orientation from that of the Zeeman and the crystal field tensors. The orientation of the zero-field tensor is correlated with some special directions in the crystal structure; the D_{zz} principal component is along the $Ca \longleftrightarrow Ca$ direction and the D_{xx} component is oriented along the perpendicular to the plane formed by three neighbouring Ca^{2+} ions.

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Preparation, characterization and catalytic properties of the microporous titanosilicate, ETS-10

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Abstract. ETS-10 is a novel large pore (12 membered ring) molecular sieve containing Ti^{4+} in O_h environment and Si^{4+} in T_d environment sharing common O^{2-} ions. As a result, ETS-10 possesses large ion-exchange and adsorption properties, besides being acidic in the H-form. We report our studies on its synthesis, characterization using SEM, IR, TGA/DTA, UV-VIS, MAS-NMR techniques, adsorption and catalytic properties.

Keywords. Titanosilicate; synthesis of ETS-10; characterization of ETS-10; catalytic properties of ETS-10.

1. Introduction

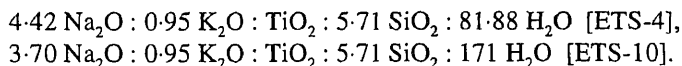
A new family of titanium silicate molecular sieves was recently discovered at Engelhard (Kuznicki 1990; Kuznicki *et al* 1991). These materials called ETS-4 and ETS-10 have unique molecular architecture due to octahedrally coordinated titanium framework ions. The structure of ETS-10 is an open three-dimensional one consisting of chains of Ti^{4+} octahedra linked to classical tetrahedral silica rings (Anderson *et al* 1994). A three-dimensional network of the interconnecting channels intersect a central pore (8 Å diameter). ETS-10 has a significant ion exchange capacity (2 Na^+ or 2 K^+ per Ti^{4+}) and the protonic form is moderately acidic.

In the present paper, we report our studies on the synthesis of ETS-10 using seeds of ETS-4, its characterization and catalytic properties in the dehydration of alcohols and isomerization of 1-butene and *m*-xylene.

2. Experimental

Synthesis of the titanosilicate (ETS-10) using seeds of ETS-4 was carried out hydrothermally using sodium silicate, titanium trichloride solution (15% solution in HCl, Loba Chemie, Bombay), sodium hydroxide, potassium fluoride dihydrate (GR Loba Chemie, Bombay) and seeds of ETS-4 (titanosilicate having small pore size 4 Å) prepared as reported earlier (Kuznicki *et al* 1991; Anderson *et al* 1994).

The molar composition of the gel in terms of oxides was as follows:



The synthesis of ETS-4 and ETS-10 were carried out as follows:

(i) *Synthesis of ETS-4 (seed)*: A solution of sodium silicate was added to NaOH with stirring. Titanium trichloride (TiCl_3 , 15% solution in HCl) was added dropwise to the above mixture and stirred for 30 min to get a blackish paste. Potassium

fluoride dihydrate ($\text{KF} \cdot 2\text{H}_2\text{O}$) was next added to the mixture and stirred for 1 h at room temperature to get a homogeneous gel ($\text{pH} \approx 11.0$). This gel was transferred to a stainless steel autoclave and capped tightly and crystallization carried out at 423 K for 5–10 days. After crystallization the solid material was filtered off and washed with deionized water. The product was then dried and identified as the crystalline small pore titanosilicate (ETS-4) with the X-ray diffraction pattern presented in figure 1A.

(ii) *Synthesis of ETS-10 using seeds of ETS-4*: A solution of sodium silicate in distilled water was mixed with NaOH with stirring. Titanium trichloride (15% solution in HCl) was then added dropwise to the above stirred gel. The paste like blackish material was allowed to stir for 30 min. $\text{KF} \cdot 2\text{H}_2\text{O}$ was next added to the above paste and stirred well. Finally ETS-4 (seed, 6.99%) was added and stirred vigorously for another 60 min till it was homogeneous ($\text{pH} = 10.8\text{--}11.0$) at room temperature. The gel was transferred to a stainless steel autoclave and crystallized at 443 K for 10 days as mentioned above. The washed crystalline product was identified as the large pore titanosilicate (ETS-10) with the X-ray diffraction pattern presented in figure 1B.

The crystalline phase identification and phase purity of the sample was verified by X-ray diffraction (Rigaku, Model D-max III). The chemical composition of the samples was determined by a combination of wet chemical methods and atomic absorption spectroscopy (Hitachi Model Z-8000). Their average particle size and morphology were determined by scanning electron microscopy (JEOL, JSM 5200). The UV-VIS diffuse reflectance spectra of the samples were obtained by using a Shimadzu (Model UV-210PC) spectrometer. FTIR spectra were recorded with a Nicolet FTIR spectrometer (Model 60XB). The solid state MAS NMR ^{29}Si and ^{23}Na were recorded at 295 K using a Bruker MSL-300 FT NMR spectrometer. Bloch decays were averaged 2400 times before Fourier transformation to obtain

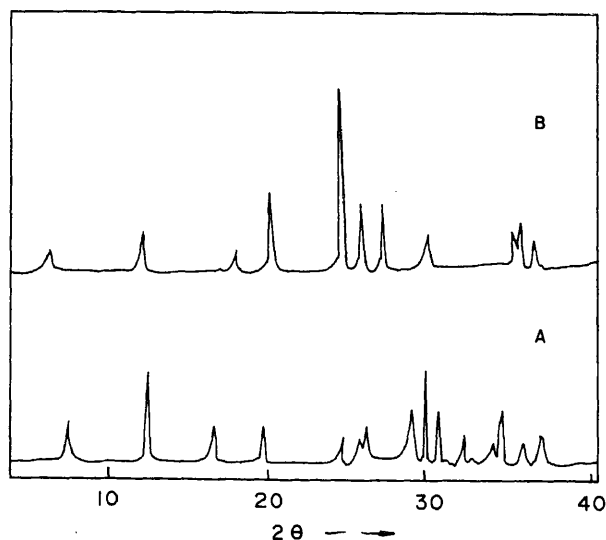


Figure 1. XRD patterns of the as-synthesized titanosilicates: (A) ETS-4 and (B) ETS-10.

spectra with sufficient S/N. While acquiring ^{29}Si spectra, a recycle time of 4 s was found to be sufficient to give fully relaxed spectra. ^{29}Si spectra were measured using TMS as the primary reference. ^{29}Si NMR spectra were recorded at $\gamma = 59.6$ MHz. An excitation pulse (t pulse) of $2\text{ }\mu\text{s}$ was used with 2000 NS (no. of scans). While acquiring ^{23}Na spectra, a recycle time of 1 s was found to be sufficient to give fully relaxed spectra. ^{23}Na spectra were measured using sodium chloride as the primary reference. ^{23}Na spectra were recorded at 79.39 MHz. An excitation pulse of $2\text{ }\mu\text{s}$ was used with 200 NS.

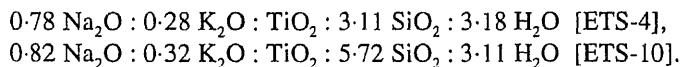
The zeolite samples of different crystallinity were also further characterized by the adsorption of different probe molecules using a vacuum (Cahn) electrobalance. Prior to sorption measurements, about 200 mg of the sample was activated at 573 K under vacuum. The ion-exchange property of the titanosilicate (ETS-10) was evaluated with 1.0 N (NaCl + KCl) mixture and then ion exchanging further with 2–3 N ammonium nitrate solution. The exchange was done under reflux for 2 h. The procedure was repeated to ensure complete ion-exchange.

The catalytically active protonic form of the titanosilicate [H-ETS-10] was obtained by repeated ion-exchange (till Na and K levels were less than 80 and 50 ppm respectively in the solid) with 1 N solution of ammonium nitrate (wt of solution/wt of zeolite = 10). The final product was filtered, dried (in an air oven at 383 K for 10 h) and calcined stepwise at 623 K for 35–40 h in a flow of nitrogen and then air.

3. Results and discussion

3.1 Synthesis of ETS-4 and ETS-10

Chemical analysis of the synthesized samples are given below:



The X-ray diffraction patterns of the titanosilicates ETS-4 and ETS-10 shown in figure 1 match very closely with those published earlier (Kuznicki 1990; Kuznicki *et al* 1991; Anderson *et al* 1994). The relative crystallinity of the sample was calculated by comparing the area of peak in the range of $2\theta = 24.65\text{--}27.5^\circ$ to that of the most crystalline reference materials (ETS-10) obtained from the same batch composition.

To study the effect of temperature on the formation of the titanosilicate, the kinetics of crystallization were studied in the range 423–473 K by comparing the extent of crystallization of the gel mixture at different intervals of synthesis time. The extent of crystallization was estimated from the ratios of the sum of the areas of the intense XRD peaks of the sample under consideration to that of the most crystalline sample obtained during the study (Domine and Quobex 1968; Tsitsishvili *et al* 1979; Chao *et al* 1981). The curves (based on XRD estimation of crystallinity) for the crystallization kinetics of ETS-10 for the gel composition mentioned earlier are presented in figure 2. The curves typically exhibit a sharp continuous rise of crystallization. The intercept made by the curve on the time axis (abscissa) is defined as the induction period (the time needed to form crystallization centers or

nuclei). In accordance with thermodynamic expectations, it is found from figure 2 that the induction period is inversely proportional to the temperature. The rate of nucleation may be assumed to be proportional to the reciprocal of the induction period and hence, it varies directly with the crystallization temperature. The induction period is followed by the rapid formation of crystalline material i.e. the rate of crystallization increases rapidly with time up to about 60–70% crystallinity and then slows down.

Linear plots were obtained when the data were fitted into Avrami–Erofeev equation (Kulkarni *et al* 1982). Applying the Arrhenius equation, the activation energy values for nucleation (E_n) and crystallization (E_c) were found out to be 76.5 and 38.3 KJ mol⁻¹, respectively. Recently shortcomings of the applicability of the above equation to zeolite crystallization data has been pointed out (Thompson 1992). He has proposed that these Avrami–Erofeev transformation kinetics should be viewed as providing only a qualitative interpretation of zeolite crystallizations. Therefore, no meaningful deductions should be drawn from these linear plots. The futility of the assumptions were explained (Den Ouden and Thompson 1992) to arrive at the rate of nucleation and crystal growth for the applicability of the Arrhenius equation to evaluate the apparent activation energies for the nucleation (E_n) and crystal growth (E_c) process.

3.2 Characterization studies

3.2a SEM analysis: SEM photographs show that the small pore titanosilicate (ETS-4) used as seed in the present study has very irregular undefined particles ranging in size from 1–8 μm (figure 3a). On the other hand, ETS-10 synthesized (with $\text{H}_2\text{O}/\text{SiO}_2 = 30$) using ETS-4 seeds (6.99 wt% based on SiO_2 input) crystallizes as sharp, twinned cuboids in the size range 1–4 μm (figure 3b).

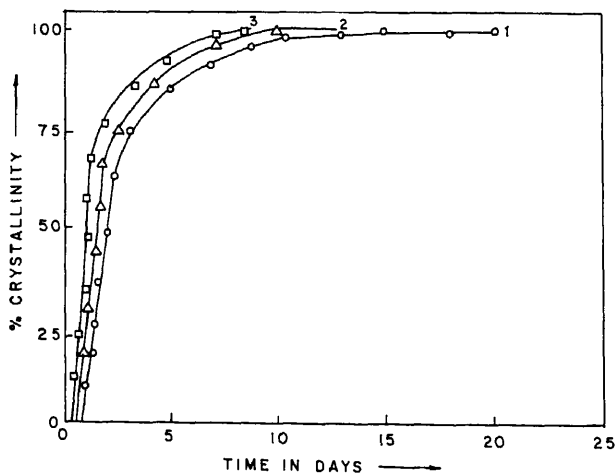


Figure 2. Effect of temperature on the kinetics of crystallization of ETS-10, Curves 1–3 correspond to 423 K, 443 K and 473 K, respectively.

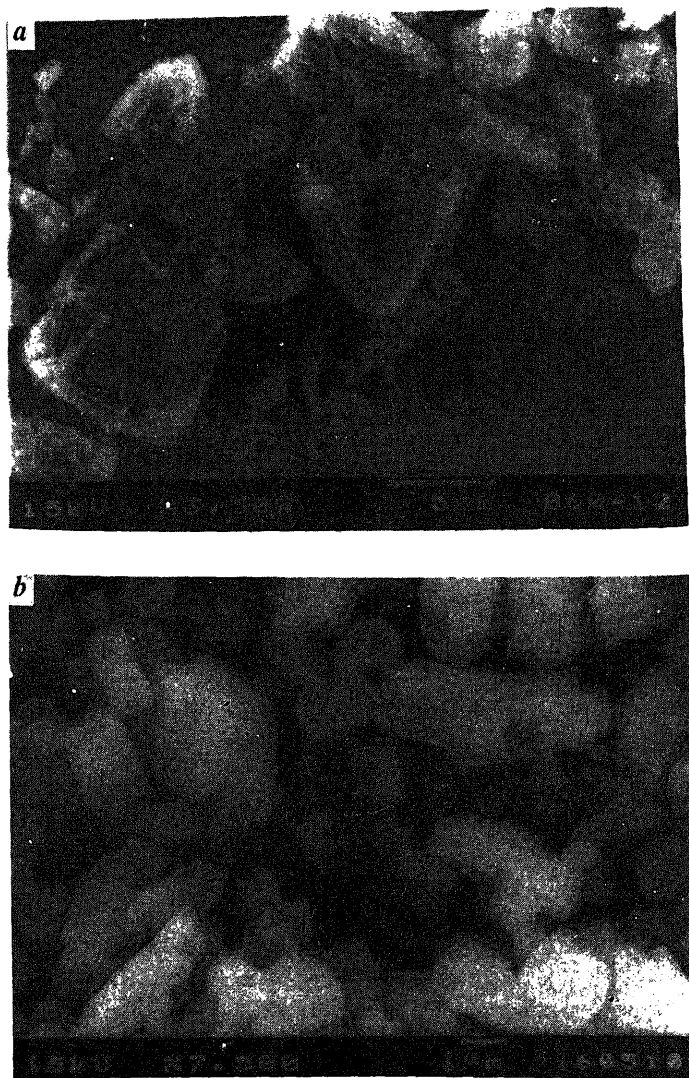


Figure 3. SEM photographs of titanosilicates: (a) ETS-4 (seed) and (b) ETS-10.

3.2b IR studies: The framework IR spectra (in the region $450\text{--}1300\text{ cm}^{-1}$) of ETS-4 and ETS-10 are shown in figure 4 (curves A and B respectively). ETS-4 shows a prominent band at 1000 cm^{-1} and two weak absorptions at 1100 and 920 cm^{-1} . The positions of the major absorption bands and shoulders corresponding to the different symmetric and asymmetric stretching vibrations (Flanigen and Khatami 1971) remained almost unchanged ($\pm 5\text{ cm}^{-1}$) for the titanosilicates prepared using seeds. The FTIR spectra of surface hydroxyl groups in dehydrated ETS-10 is shown in figure 5. The peak around 3735 cm^{-1} is due to isolated terminal silanol groups (Chandwadkar *et al* 1993). The sharp peak at 3700 cm^{-1} observed on ETS-10

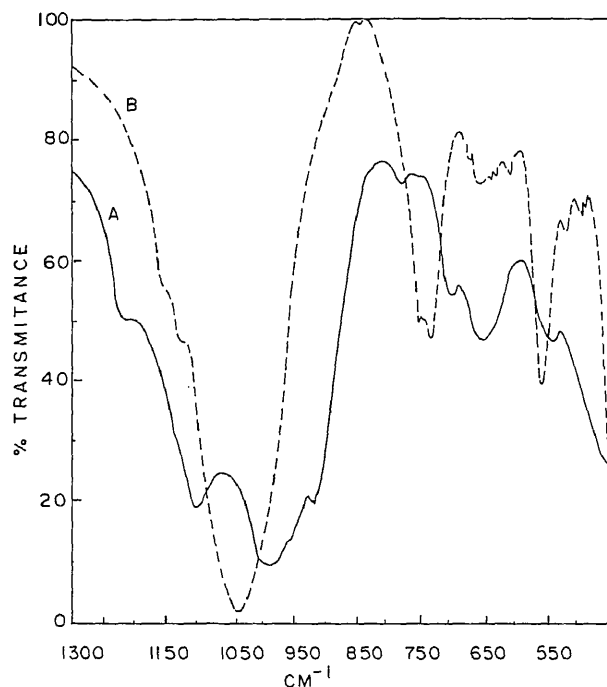


Figure 4. IR framework vibration spectra of the titanosilicates; (A) ETS-4 and (B) ETS-10.

probably is due to isolated Ti-OH groups. The broad band around $3200\text{--}3600\text{ cm}^{-1}$ is probably due to H-bonded surface hydroxyl groups of both Si and Ti.

3.2c TGA/DTA: The thermal behaviour of ETS-10 is shown in figure 6. The endotherm at 393 K is due to the loss of physically sorbed or occluded water, and at $\sim 963\text{ K}$ may be due to the dehydration of terminal -OH groups. The two exotherms with peak maxima at 573 and 723 K are probably due to phase transitions.

3.2d UV-VIS (DRS): The diffuse reflectance spectra in the UV-VIS region of ETS-10 and ETS-4 are presented in figure 7 (curves a and b respectively). The broad absorption in the region 250–320 nm suggest the presence of Ti^{4+} in O_h co-ordination (Jacobs 1992).

3.2e MAS-NMR: The ^{29}Si NMR spectrum of ETS-10 (figure 8A) shows three sharp bands at $\delta = -94.4(1)$, $-96.8(2)$ and $-103.8(3)$ ppm, indicating the presence of at least three different Si environments in ETS-10. The weak band at $\delta = -90.74$ ppm (marked by an arrow) is probably due to ETS-4 present as an impurity in the sample as this band was prominent in the case of pure ETS-4. Further this band disappeared after calcination at 623 K.

The ^{23}Na NMR spectrum (figure 8B) shows the presence of two resonance bands at $\delta = 9.17(1)$ and $-9.90(2)$ ppm corresponding to their presence in two different environments (Engelhardt and Michel 1987).

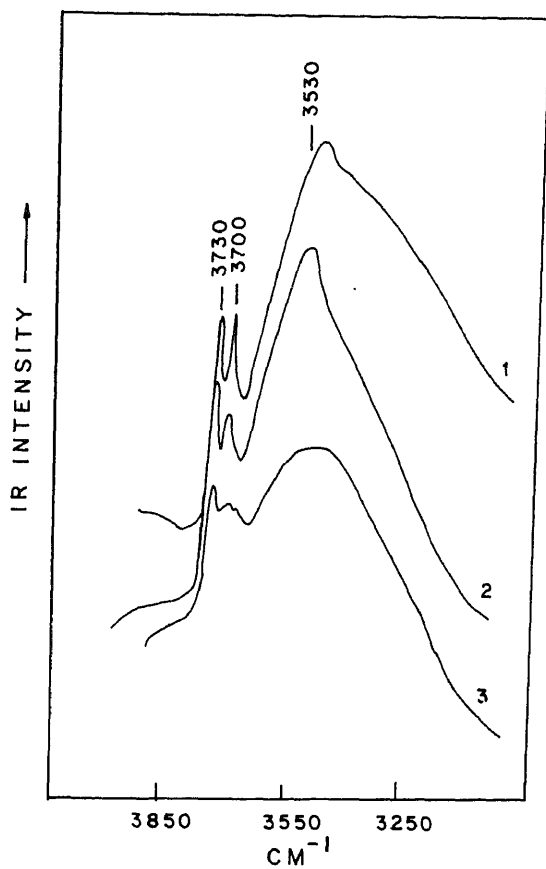


Figure 5. FTIR spectra of ETS-10 recorded at 313 K, 373 K and 473 K (curves 1–3 respectively).

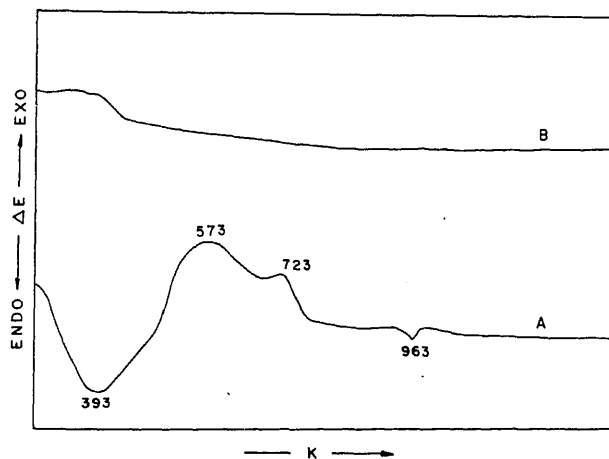


Figure 6. Thermoanalytical curves of ETS-10: (A) DTA and (B) TGA.

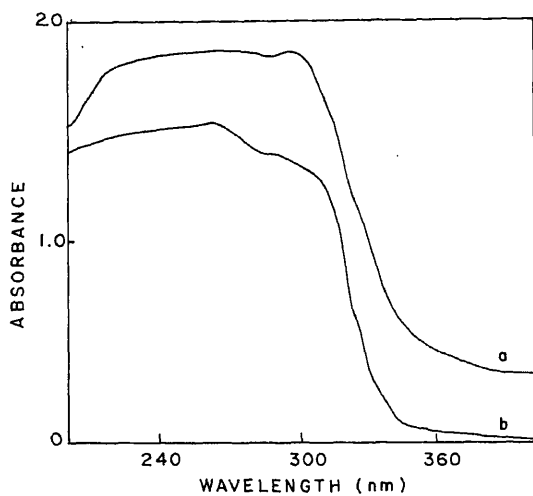


Figure 7. UV-VIS diffuse reflectance spectra of titanosilicate samples: (a) ETS-10 and (b) ETS-4.

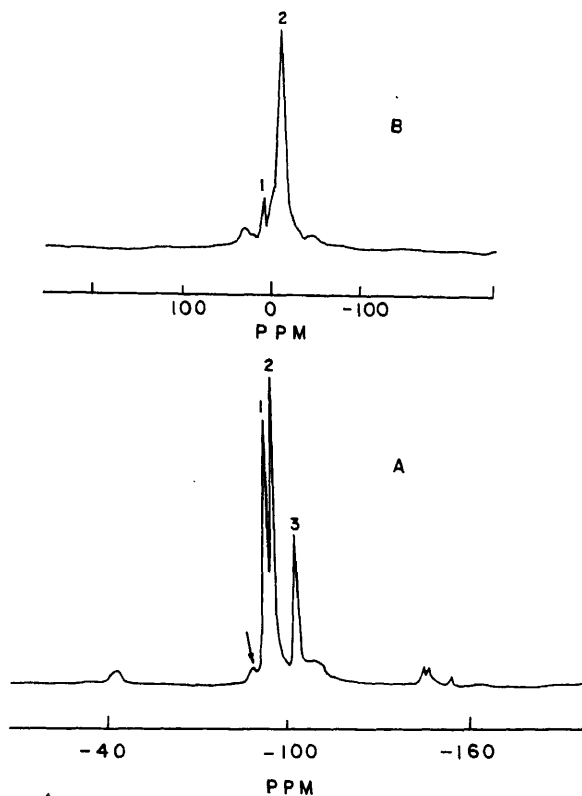


Figure 8. ^{29}Si and ^{23}Na MAS-NMR (curves A and B, respectively) of ETS-10.

3.2f Sorption studies: The sorption isotherms for water, *n*-hexane and 1,3,5-trimethylbenzene obtained at 298 K at a $p/p_0 = 0.5$ are presented in figure 9. The large adsorption capacity for water shows that the molecular sieve is hydrophilic in nature. Besides, the rapid adsorption in large amounts of 1,3,5-trimethylbenzene (diameter = 8.4 Å) confirms that ETS-10 has pores of diameter of at least 8 Å.

3.3 Catalytic studies

3.3a Alcohol dehydration: H-ETS-10 is active in the dehydration of alcohols. In the case of dehydration of alcohols it decreases in the order: *t*-butanol > cyclohexanol > isobutanol > 2-butanol > 1-butanol. The order of reactivities follows the same trend as the stabilities of the carbenium ions formed from them. The primary product of dehydration of isobutanol isomerizes further into 1- and 2-butenes. However, the isomerization is not significant when *t*-butanol is dehydrated. The dehydration of cyclohexanol leads mainly to cyclohexene and methyl-cyclopentenones (MCP⁺), the latter products being formed by the skeletal rearrangement of cyclohexene (table 1).

3.3b Isomerization: ETS-10 isomerizes 1-butenes, with the formation of large quantities of saturated compounds (butanes 57%). This shows that ETS-10 possess good hydrogen transfer activity. The excess hydrogen probably comes from the carbonaceous residues which were also formed in significant quantities.

The conversion of *m*-xylene over ETS-10 is moderate (16.4%). The low I/D ratio (isomerization/disproportionation ≈ 0.5) shows that not only are the pores of ETS-10 large but also its acid site density is very high leading preferentially to bimolecular disproportionation reactions instead of isomerization reactions (table 2). High acid

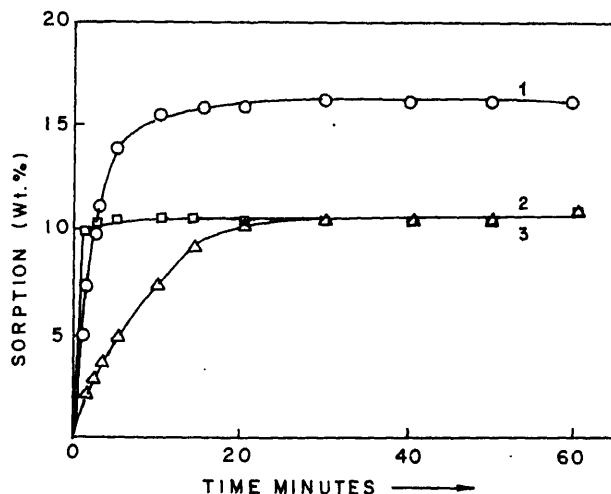


Figure 9. Sorption isotherms of H₂O, *n*-hexane and 1,3,5-trimethylbenzene (curves 1, 2 and 3 respectively) obtained over ETS-10.

Table 1. Dehydration of alcohols over ETS-10.

	1-butanol	2-butanol	Isobutanol	<i>t</i> -butanol	Cyclohexanol
Conv. (%)	87.9	90.6	99.9	99.9	99.9
Products wt. (%)					
<i>i</i> -Butene	0.11	1.4	1.2	0.18	—
Butene-1	17.2	7.2	10.4	—	—
<i>i</i> -Butene	2.5	48.0	54.5	98.8	—
<i>n</i> -Butane	0.5	0.24	0.22	—	—
<i>t</i> -Butene-2	36.8	15.5	17.7	0.26	—
<i>c</i> -Butene-2	28.1	11.9	13.7	0.2	—
Cyclohexene	—	—	—	—	80.1
MCP*	—	—	—	—	18.4
C ₁ -C ₃ and others	2.7	6.4	2.1	0.5	0.9

Temp.: 573 K, WHSV: 2 (h⁻¹), N₂: (5 ml/min), Press.: 1 atm. TOS: 1 h

*Methyl cyclopentenenes.

Table 2. Isomerization activities of ETS-10.

1-Butene		<i>m</i> -Xylene	
Conv. (%)	98.6	Conv. (%)	16.4
Products wt. (%)		Products wt. (%)	
C ₁ -C ₃	6.9	Benzene	1.9
<i>i</i> -Butane	43.5	Toluene	4.1
<i>i</i> -Butene	2.8	<i>p</i> -Xylene	1.0
<i>n</i> -Butane	13.3	<i>o</i> -Xylene	3.3
<i>t</i> -Butene-2	2.6	1,3,5 TMB*	1.3
<i>c</i> -Butene-2	1.8	1,2,4 TMB*	3.6
<i>i</i> -Pentane	18.7	1,2,3 TMB*	0.4
Others	9.0	Others	0.8

Temp.: 573 K, WHSV: 1 (h⁻¹), N₂: (5 ml/min), Press.: 1 atm. TOS: 1 h

*Trimethylbenzenes.

site density is due to the fact that concentration of the Ti⁴⁺ ions is high and each Ti⁴⁺ ion can lead to two acid sites.

4. Conclusions

ETS-10 can be suitably synthesized using ETS-4 as seeds. Infrared and UV-VIS(DRS) studies show that the Ti⁴⁺ ions are in O_h symmetries in ETS-10 as reported by earlier workers. Adsorption studies reveal that the molecular sieve is hydrophilic and has pores of diameter of at least 8 Å. ETS-10 is found to be active in the dehydration of alcohols and the isomerization of 1-butene and *m*-xylene.

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New galvanic cell designs for minimizing electrode polarization

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Abstract. New galvanic cell designs, incorporating one or two buffer electrodes, are developed to minimize the electrode polarization caused by electrochemical permeability of the electrolyte at high temperature. When a nonpolarizable reference electrode is employed, a cell with three-electrode compartments can be used to measure the chemical potential of oxygen in two-phase fields of ternary systems, associated with one degree of freedom at constant temperature. A buffer electrode is placed between the reference and measuring electrodes. The buffer electrode, maintained at approximately the same oxygen chemical potential as the measuring electrode, absorbs the semipermeability flux of oxygen between reference and measuring electrodes.

When the reference electrode is polarizable, two buffer electrodes are required between the reference and measuring electrodes. The reference and reference-buffer electrodes have the same chemical potential of the active species. Similarly the measuring electrode and its buffer are of approximately the same chemical potential. A significant chemical potential difference exists only between the two buffers, which may become polarized due to coupled transport of ions and electronic defects through the electrolyte. Since the reference and measuring electrodes are insulated, the emf of the solid state cell is unaffected. The use of the buffer electrode designs permit more accurate thermodynamic measurements on metal and ceramic systems at high temperature.

Keywords. Electrode polarization; semipermeability flux; buffer electrode; solid electrolyte cells.

1. Introduction

Solid state galvanic cells have been extensively used for high temperature thermodynamic studies on materials (Pratt 1990). An important factor which is often responsible for incorrect measurement of chemical potential when using a solid state galvanic cell is electrode polarization. Polarization occurs as a result of physical or electrochemical permeability of the solid electrolyte. While physical permeability can be reduced by using a dense form of the solid electrolyte, free from interconnecting porosity, electrochemical permeability results from the intrinsic properties of the material. When the difference in the chemical potential of active species such as oxygen between the measuring and reference electrodes is substantial, there is always a small flux of this species through the electrolyte separating them, even in the absence of physical porosity (Fouletier *et al* 1976). The electrochemical permeability is caused by the coupled transport of oxygen ions and electrons or holes in an oxide solid electrolyte under the oxygen potential gradient. This flow of oxygen can be stopped only by opposing it with an external d.c. voltage, equivalent to the oxygen chemical potential difference (Jacob and Jeffes 1971). Unless the electrochemical reactions at the electrodes are sufficiently rapid, the flux of oxygen can lead to polarization of the electrodes. In this article new designs of galvanic cells are suggested that minimize the effect of polarization. The new

designs permit extremely accurate thermodynamic measurements at high temperature, unparalleled by any other technique currently available.

When gas electrodes are used, the presence of polarization manifests as flow rate dependence of emf. Although polarization can be reduced by increasing the flow rate, a practical limit is set by the cooling effect of the streaming gas. Asymmetrical gas flows at the two electrodes can result in differential cooling and non-isothermal contributions to cell emf which are difficult to correct.

There have been few earlier attempts to minimize polarization in high temperature galvanic sensors. The idea of deflecting the electrochemical flux of oxygen by a zirconia point electrode configuration was suggested by Fouletier *et al* (1976). The design of the point electrode is illustrated in figure 1. The platinum lead electrode actually measures the chemical potential in a 'microsystem' formed at the triple phase region between the electrode, electrolyte and gas. The oxygen flux through the electrolyte due to electrochemical semipermeability may alter the equilibrium oxygen chemical potential in the microsystem, if the exchange kinetics between the gas phase and the microsystem does not keep pace with the semipermeability flux. The point electrode deflects the oxygen flux away from the 'microsystem' at the triple phase contact. Since the ionic flux takes the lowest resistance path, this flux is dissipated at the tip of the point electrode made using the same material as the electrolyte. The measured composition of the gas at the platinum lead is unaffected and corresponds to that of the bulk gas. Jacob *et al* (1982) have shown that the performance of the point electrode can be improved by applying a porous coating of a catalyst such as Pt at the tip of the point electrode made from the solid electrolyte material. The catalyst helps to dissipate the flux faster at the tip.

Mallika *et al* (1986) proposed a design in which a solid electrolyte, a buffer electrode and a point electrolyte are interposed between the reference and test electrodes, as shown in figure 2. The buffer electrode absorbs the flux arriving from the reference electrodes. However, the buffer electrode has an oxygen chemical potential intermediate between the reference and the test electrodes. The buffer and the test electrodes are separated by a point electrode, made of an ionic conductor.

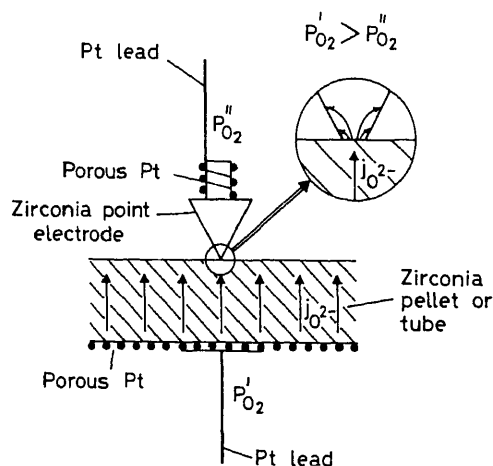


Figure 1. A schematic representation of the point electrode for deflecting the semipermeability flux from the measuring electrode (after Fouletier *et al* 1976).

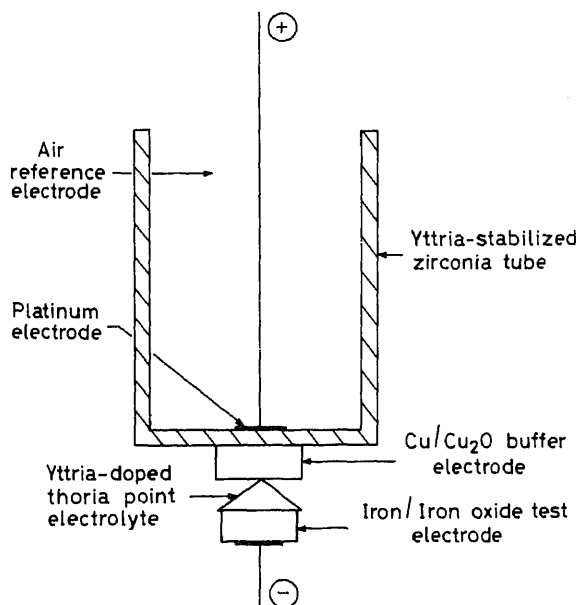


Figure 2. Schematic of triple electrode-bielectrolyte cell arrangement (after Mallika *et al* 1986).

In this design, the point electrode does not deflect the flux. However, it reduces the contact area between the buffer and the solid electrolyte, and reduces the flux between the buffer and test electrode. The major disadvantage of their design is that both the buffer and the measuring electrodes are exposed to a common gas phase. The transfer of oxygen between the electrodes via the gas, mediated by the presence of the trace concentrations of H_2O , CO and CO_2 in the inert gas blanket, can significantly affect the emf.

Lundberg and Rosén (1992) proposed another design of a galvanic cell, shown in figure 3, with a gas buffer electrode maintained at the same chemical potential of the measuring electrode. They used two solid electrolyte tubes, one containing the solid reference electrode, and the other containing the condensed phase test electrode. Pt leads connected to the outside of each solid electrolyte tube were joined. The oxygen partial pressure in the inert gas phase between the two solid electrolyte tubes was maintained at the same value as that in the measuring electrode. This was achieved by placing a large amount of the measuring electrode mixture in the proximity of the solid electrolyte tubes, but without physical contact. The design avoids the polarization of the measuring electrode, but does not necessarily prevent the polarization of the reference electrode. To overcome the drawbacks of the earlier arrangements, new designs are proposed and their efficacy tested.

2. Design of a galvanic cell with three compartments

2.1 Principle

When a nonpolarizable reference electrode is employed, a cell design with three

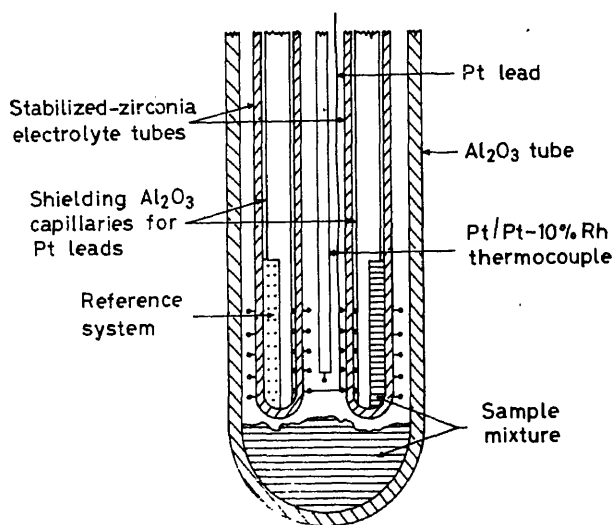


Figure 3. Design of a galvanic cell with a gas buffer electrode (after Lundberg and Rosen 1992).

electrode compartments can be used to avoid polarization of the measuring electrode. A buffer electrode, identical to the measuring electrode, is placed between the reference and the measuring electrodes. Thus there is no flux between the buffer and the measuring electrode as their chemical potentials are the same. The buffer essentially insulates measuring electrode from polarization. Since the reference electrode is nonpolarizable, and the measuring electrode is protected from polarization, the cell emf is unaffected by the electrochemical flux of oxygen through the intervening solid electrolyte. Pure oxygen, at a fixed pressure, constitutes a nonpolarizable electrode. It also serves as a primary standard for oxygen potential. Other multiphase electrodes, associated with high exchange currents or fast reaction rates, may also function as nonpolarizable electrodes under narrowly specified conditions.

If an electrode is composed of a chemically invariant system at constant temperature and pressure, and the electrode reactions are sufficiently rapid, the semipermeability flux of oxygen does not generally alter its chemical potential. Experimentally, the effect of semipermeability flux on emf can be minimized by taking a greater amount of the phase that is consumed by the flux at each of the solid electrodes (Jacob and Mathews 1990). Electrochemical techniques for the measurement of oxygen potential of an invariant system at constant temperature are reasonably well established (Pratt 1990). However, measurements on systems that have one or more degrees of freedom are more difficult, especially if the phases involved are solids. The composition of the solid at the electrode-electrolyte interface may be altered by minor perturbations such as oxygen leakage, physical or electrochemical.

A system with one degree of freedom at experimental temperatures was encountered in the study of the ternary Mn-Rh-O (Jacob and Sriram 1994). Phase diagram for the system is shown in figure 4. Metallic Rh coexists with the spinel solid solution $\text{Mn}_{1-2x}\text{Rh}_{2x}\text{O}_4$. This two-phase equilibrium in the ternary system is associated with one degree of freedom. The equilibrium partial pressure of oxygen can vary with

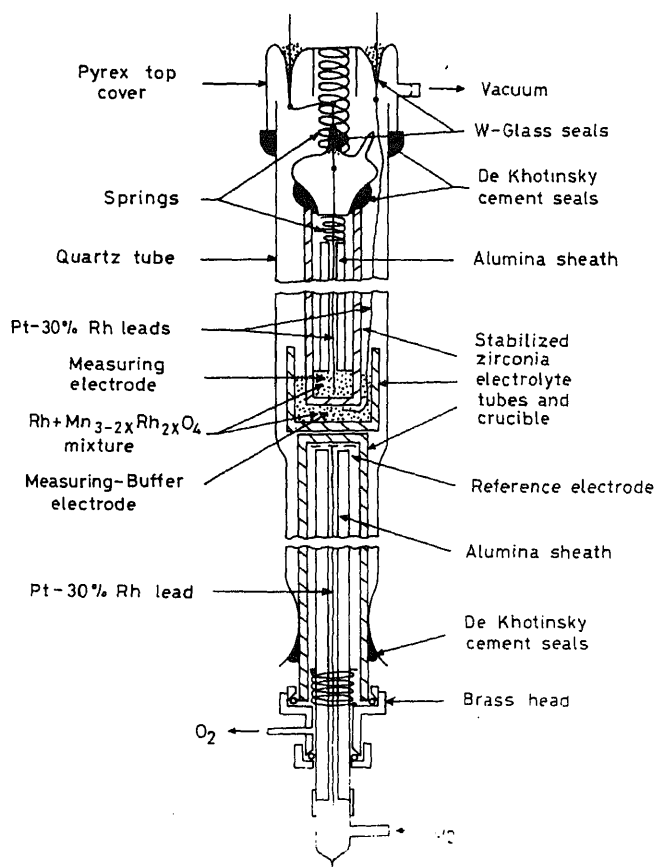
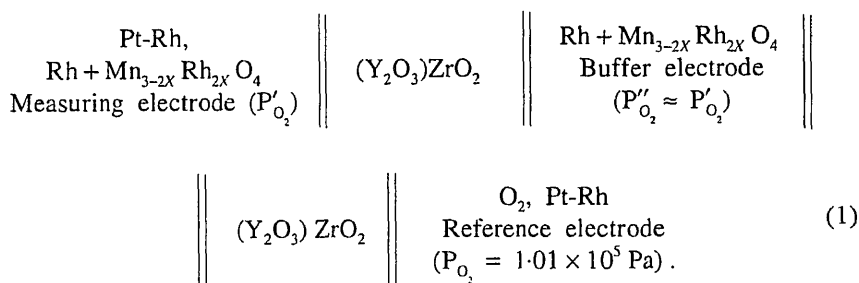


Figure 4. Schematic diagram of the three-electrode system (cell 1) for emf measurement.

the composition of the spinel solid solution at constant temperature. To measure the thermodynamic mixing properties of the solid solution, it is necessary to determine the composition dependence of the partial pressure in the two-phase region.

Initial measurements on two-phase equilibria using the conventional two-compartment arrangement (Kale and Jacob 1992) with physical separation of the two electrodes by a long solid electrolyte tube, were not successful. The emf was found to drift gradually with time. The drift was reduced, when a sealed system, suggested by Charette and Flengas (1968), was employed. The interaction with the gas phase was minimized in a closed system. However, the drift could not be suppressed completely. The electrochemical flux of oxygen through the electrolyte was found to change the composition of the spinel solid solution at the electrode/electrolyte interphase.

To make accurate measurements, a cell design shown in figure 5 was used (Jacob and Sriram 1994). It consisted of three distinct compartments, separated by two



The measuring and reference electrodes were contained inside two separate zirconia tubes. The measuring electrode consisted of an intimate mixture of Rh and $\text{Mn}_{3-2X}\text{Rh}_{2X}\text{O}_4$ powders in equimolar ratio. The mixture was rammed against the closed end of a stabilized-zirconia tube with a Pt-30% Rh lead embedded in the mixture. An alumina sheath was used to insulate this lead and to press the measuring electrode against the zirconia tube. The top of the zirconia tube was sealed with De Khotinsky cement to a bell-shaped pyrex tube, which supported a W electrode connection sealed into the glass. The assembled measuring electrode half-cell was first evacuated using a side arm tube, heated to ~ 400 K, and then the tube was flame-sealed under vacuum.

The measuring half-cell assembly rested on a buffer electrode contained in a stabilized-zirconia crucible. The buffer also consisted of a mixture of Rh and $\text{Mn}_{3-2X}\text{Rh}_{2X}\text{O}_4$, but the spinel phase was slightly richer in Mn_3O_4 than in the measuring electrode. Thus the partial pressure of oxygen in the buffer was slightly less (~ 15 mV) than that of the measuring electrode. The buffer electrode was prepared by consolidating an intimate equimolar mixture of constituent phases in the zirconia crucible, with a Pt-30% Rh lead embedded in the powder.

The zirconia crucible rested on another inverted zirconia tube, through which pure oxygen gas was passed at a pressure of 1.01×10^5 Pa and a flow rate of 3 ml s^{-1} . The pressure inside the tube was controlled by a cascade of bubblers placed at the gas exit. The oxygen electrode served as the reference. The mating surfaces of the crucible and the tube were polished with diamond paste to minimize contact resistance. The inside surface of the inverted tube was platinized. A Pt gauze was pressed against the closed end of the inverted tube using an alumina sheath. A Pt-30% Rh lead, spot-welded to the gauze, was passed through the alumina sheath. The open end of the tube was fitted with a brass-head.

The cell was then assembled inside a fused quartz enclosure as shown in figure 5. All electrode connections were silver soldered. The outer quartz enclosure was also evacuated from a side arm tube and flame-sealed under vacuum. The top half of the cell assembly shown in figure 5, was identical to that developed by Charette and Flengas (1968). The entire assembly was placed inside a vertical resistance furnace, with the electrodes located in the even-temperature zone (± 1 K). The upper and the lower parts of the assembly, where cement seals were located, remained at room temperature during measurement. A Faraday cage made from stainless steel foil was placed between the furnace and the cell assembly. The foil was grounded to minimize induced emf on cell-leads. The temperature of the furnace was controlled to ± 1 K. The cell potentials were measured with a high impedance digital voltmeter.

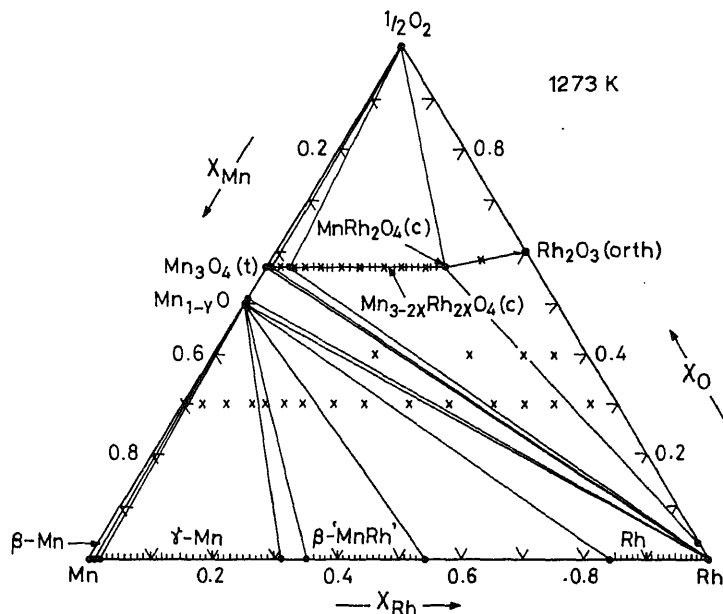
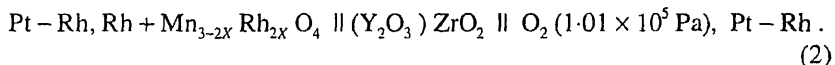


Figure 5. Phase relations in the system Mn-Rh-O at 1273 K. The compositions of the samples analyzed are shown by x (after Jacob and Sriram 1994).

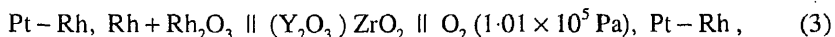
The potential readings were corrected for small thermal emfs, measured separately.

As the cell potential of the three-electrode assembly is determined only by the chemical potentials of oxygen in the measuring and reference electrodes, the effective cell can be concisely written as:

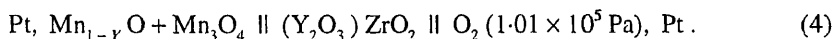


The cell is written such that the right-hand electrode is positive.

Chemically invariant two-phase mixtures at constant temperature and pressure in binary systems were also measured using 'three-compartment design' of the cell. Studies were conducted on cells:



and



The measuring and buffer electrodes in these cells had identical composition.

2.2 Results and discussion

The reversible emf of cell (1) is shown as a function of temperature in figure 6 for different compositions of the oxide solid solution. The reversibility of the emf

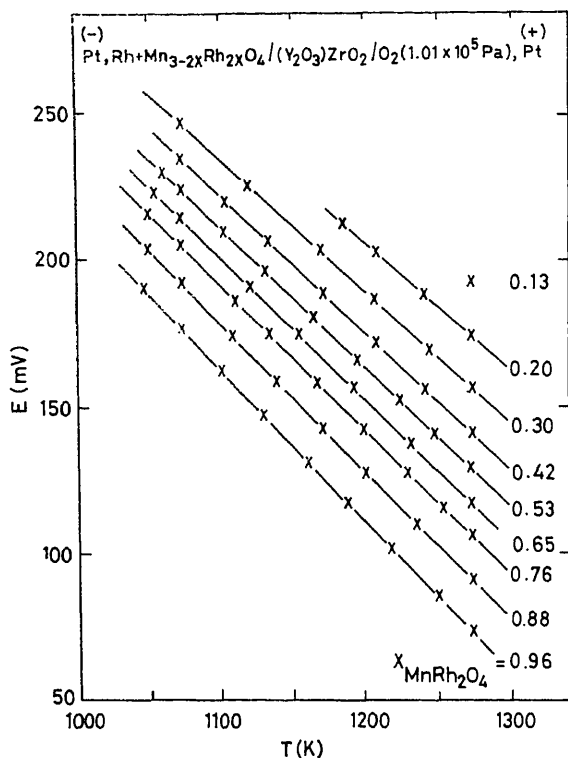


Figure 6. Temperature dependence of the emf of cell (1) for different compositions of the solid solution.

was checked by microcoulometric titration in both directions. A small quantity of current ($\sim 50 \mu\text{A}$ for 300 s) was passed through the cell using an external potential source. The open circuit emf was then monitored as a function of time. After each such titration, the emf returned to the original value before titration, thus ensuring cell reversibility. The emf was not affected by the flow rate of oxygen through the reference electrode in the range $2\text{--}5 \text{ ml s}^{-1}$.

With the 'three-electrode design' of the cell, the emfs were steady ($\pm 0.3 \text{ mV}$) for periods in excess of 30 ks. The buffer electrode contained a solid solution with the next lower concentration of MnRh_2O_4 than the measuring electrode. The emf of the buffer electrode against the reference was higher by $10\text{--}18 \text{ mV}$ than that of the measuring electrode at the start of each experiment. As a consequence of the flux of oxygen from the reference electrode, the emf of the buffer-electrode gradually decreased to a value $\sim 15 \text{ mV}$ lower than that of the measuring electrode by the end of the experiment. This clearly demonstrates the need for the buffer to absorb the oxygen flux and protect the measuring electrode from being disturbed. The emf between the buffer and measuring electrodes is a direct measure of polarization.

Studies on cells (3) and (4) indicate that the difference between the emf of the buffer and the measuring electrode increases from a value of zero at the beginning of the experiment to a maximum value of $\sim 3.5 \text{ mV}$ at the end. Thus the semipermeability

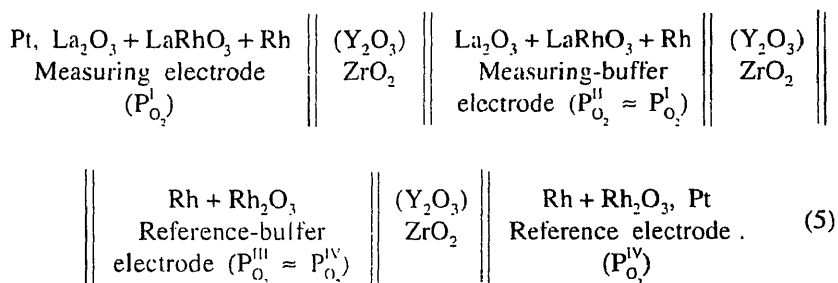
flux of oxygen from the oxygen reference through the solid electrolyte does not appear to significantly change the chemical potential of systems that are invariant under the experimental conditions. Nevertheless, use of a buffer is recommended for very precise measurements of invariant equilibria in the future, especially when the driving force for oxygen transport is large. Such situations are encountered when pure oxygen or air is used as a reference electrode and measurements are made on systems with low oxygen chemical potential.

3. Design of a galvanic cell with four compartments

3.1 Principle

The 'three-compartment cell' design does not completely solve the polarization problem unless one of the electrodes is nonpolarizable. When the reference electrode is also polarizable, two buffer electrodes are required between the reference and measuring electrodes. To protect the reference electrode from polarization, a reference-buffer electrode, identical to the reference electrode is interposed. Thus, in the absence of a driving force, there is no transport of the active species between the reference-buffer and reference electrodes. Similarly, the measuring electrode is also insulated using a buffer of approximately same chemical potential. The chemical potential difference exists between the two buffers, which may become polarized due to coupled transport of ions and electronic charge carriers through the electrolyte separating them. During the course of experiment, the oxygen chemical potential of the buffer electrodes may thus change from their initial values. The cell emf, which is related to the oxygen chemical potential difference between the measuring and the reference electrodes, is unaffected.

The use of a four-compartment cell design permits more accurate thermodynamic measurements on metal and ceramic systems at high temperature. A four-compartment galvanic cell was used for accurate thermodynamic measurements on LaRhO_3 at high temperature (Jacob and Waseda 1995). The cell consisted of four distinct compartments, separated by yttria-stabilized zirconia tubes and crucibles. The cell, schematically depicted in figure 7, can be represented as:



The reference electrode was prepared by compacting an intimate mixture of Rh and Rh_2O_3 in the molar ratio 1 : 1.5 against the closed end of yttria-stabilized zirconia tube, with a Pt-30% Rh lead embedded in the mixture. The reference-buffer electrode was prepared in an identical fashion using a stabilized-zirconia tube of

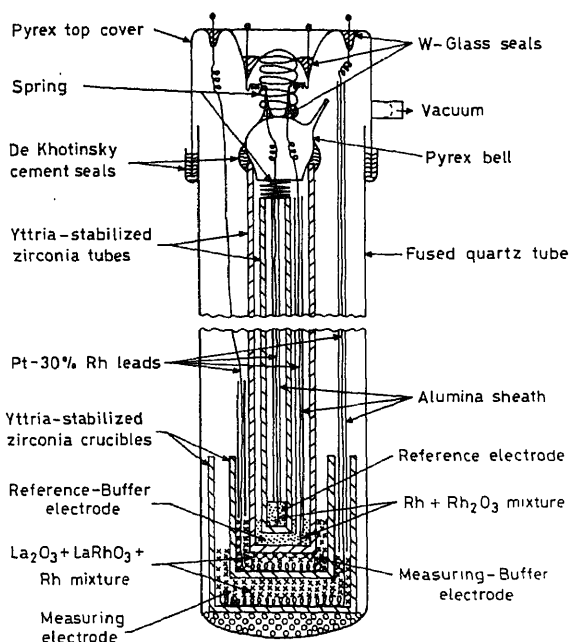
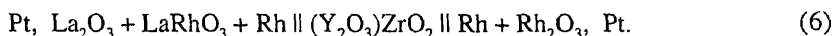


Figure 7. A schematic representation of the four-compartment cell arrangement for emf measurement.

larger diameter. The smaller zirconia tube containing the reference electrode was placed inside the larger tube.

The measuring electrode was prepared by compacting a mixture of La_2O_3 , LaRhO_3 and Rh in the molar ratio 1 : 1.5 : 1 in a stabilized-zirconia crucible, with a Pt-30% Rh lead buried in it. The measuring-buffer electrode was prepared in the same way inside a crucible with smaller diameter. The larger zirconia tube containing the reference-buffer electrode was placed over the measuring-buffer electrode in the smaller crucible, and the space between them was filled with the three-phase electrode mixture. The compartments were assembled as indicated in figure 7, following a procedure similar to that described in the earlier section.

As the cell potential of the four-electrode assembly is determined only by the chemical potentials of oxygen in the measuring and reference electrodes, the effective cell can be concisely written as:



Again, the cell is written such that the right-hand electrode is positive.

3.2 Results and discussion

The reversibility of the emf of cell (5) was established by microcoulometric titration in both directions. The emf measured between the two buffer electrodes was always

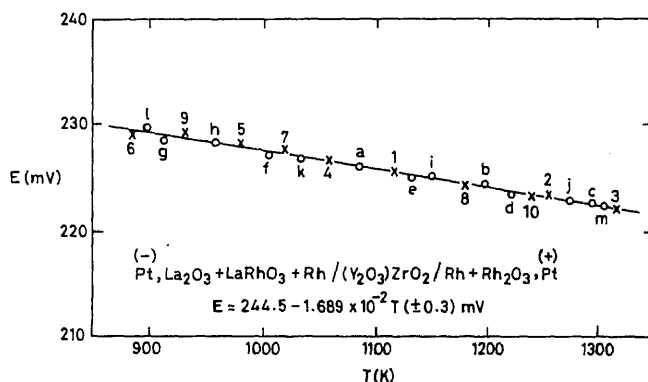


Figure 8. Temperature dependence of the emf of cell (5).

lower by 2 to 3.5 mV than that between the measuring and reference electrodes. When microcoulometric titration was done between the buffer electrodes, there was a small hysteresis effect of ~ 2 mV. This indicated a finite polarization effect due to the flux of oxygen from the reference-buffer to the measuring buffer electrode. Although both electrode systems are invariant at constant temperature, measurement of their oxygen potential using the conventional solid state cell can result in a small but significant systematic error. The use of the four-compartment design improves the accuracy by insulating the measuring and reference electrodes from polarization effects.

The reversible emf of cell (5) is shown in figure 8 as a function of temperature. Emf was found to be reproducible on temperature cycling. The standard Gibbs free energy change for the overall cell reaction:



$$\Delta G_f^\circ = -141,560 + 9.78 T (\pm 180) \text{ J mol}^{-1}, \quad (8)$$

is obtained directly from the emf. There are no data in the literature with which these values can be compared.

4. Summary

The application of buffer electrodes is investigated for minimizing electrode polarization in high temperature solid state galvanic cells. In the absence of physical porosity, the polarization is caused by the electrochemical permeability, which results from the coupled transport of the mobile species and electronic charge carriers in the solid electrolyte under a chemical potential gradient. When a nonpolarizable reference electrode is employed, a cell with three-electrode compartments can be used to insulate the measuring electrode from electrode polarization. The buffer electrode, introduced between the reference and the measuring electrodes, acts as a sink for the electrochemical flux and prevents it from reaching

the measuring electrode. The polarization problem is not completely solved in a three-compartment cell design unless one of the electrodes is nonpolarizable. Two buffer electrodes are required between the reference and measuring electrodes when both the electrodes are susceptible to polarization effects. In a four-compartment cell design, accuracy of measurement is improved by insulating both the electrodes using buffers. The use of a buffer permits precise thermodynamic measurements on metal and ceramic systems at high temperature, especially for systems with one or more degrees of freedom at constant temperature.

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Development of indigenous technology for production of titanium sponge by the Kroll process

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Abstract. Titanium has emerged as a major structural metal for a wide range of industrial applications due to its attractive engineering properties. India has a large and rich reserve base for this metal in the beach sands of the eastern and southern regions with well established production facilities for their separation into individual minerals. Research and Development activities for establishing the metal production technology have been underway in the country for over two decades. The Defence Metallurgical Research Laboratory, Hyderabad, has already demonstrated the metal production technology by the conventional Kroll process on 2000 kg/batch scale and is now all set for demonstrating the same by the more advanced, energy efficient combined process route on 4000 kg/batch scale. The paper reviews the R & D efforts undertaken so far in the field of metal extraction with emphasis on the current status of this developmental activity at DMRL.

Keywords. Titanium; Kroll process; combined process; magnesium; mono polar cell; multi polar cell.

1. Introduction

Titanium is the fourth most abundant structural metal after aluminium, magnesium and iron. Its unique engineering properties especially the high specific strength and outstanding corrosion resistance make it the most preferred metal for a variety of applications in a wide spectrum of industries such as the aerospace, power generation, chemical and petrochemical, paper and pulp, marine and ship building etc. Though started as an aerospace material, the metal has now reached the status of a common metal in the developed countries like Japan and the US owing to its impressive and useful properties. Titanium is also emerging as an ecofriendly metal due to its usage in the construction of antipollution equipment especially in the chemical and automobile industry.

In the earth's crust, titanium is mostly found in the form of oxide minerals viz. rutile (TiO_2) and ilmenite (FeOTiO_2). Due to the high thermodynamic stability of titanium oxides, attempts to prepare the metal directly from oxide have not been successful and the metal extraction through the chloride route is widely practised by the industry. Among various processes to prepare titanium metal from titanium tetrachloride, three processes viz. (i) the Hunter's sodium reduction, (ii) the Kroll's magnesium reduction and (iii) the fused salt electrolysis of TiCl_4 , gained industrial significance. Out of these the Kroll's process of reducing titanium tetrachloride with liquid magnesium has gained wider industrial acceptance because of its technical viability for production of sponge in larger, commercial size batches and the relative

concentrates. Thus, the Kroll process has emerged as the major metal extraction process for economic production of titanium sponge on industrial scale and currently over 97% of the world capacity is exclusively by this route. The Kroll sponge production technology involves the following process steps: (i) preparation of TiCl_4 by chlorination of oxide concentrates, (ii) reduction of TiCl_4 by magnesium, (iii) separation of Mg/MgCl_2 from the reaction mass and (iv) mechanical processing of sponge to a final size required for the subsequent ingot melting.

During the last two decades there have been many breakthroughs and innovations in the Kroll technology resulting in large scale production of the metal much more economically than ever before. While the development of fluidized bed chlorination revolutionized the tetrachloride production, the advent of combined process lead to production of superior quality sponge on larger size batches resulting in lower specific power consumption for metal production. The development of multipolar cell for magnesium electrolysis has also contributed in a significant way for the economic production of titanium sponge because of the reduced MgCl_2 recycling costs.

India has more than one reason to go in for commercial production of the metal titanium. Annually, considerable amount of valuable foreign exchange is being spent on import of copper and nickel. The country has the opportunity to come out of this situation due to the fact that many copper and nickel alloy components can be replaced with titanium. Further, the country has a rich and large mineral base for titanium with our ilmenite and rutile reserves estimated at 140 and 8 million tonnes, respectively. Keeping in view the strategic nature of the metal (based on critical dependence of the Aerospace and Defence related industries on titanium), it is too risky to rely on sponge imports. Also, the country has all the production facilities starting from mineral beneficiation to the manufacture of titanium mill products except for sponge production.

2. Development of metal production technology in the country

Laboratory studies on TiCl_4 and titanium sponge preparation by magnesium, sodium and fused salt electrolysis were initially carried out at BARC, Bombay in the 1960s (Sridhar Rao *et al* 1969; Ahluwalia *et al* 1973). Pilot plant investigations carried out at the Nuclear Fuel Complex, Hyderabad during 1970s on sodium reduction and magnesium reduction on 100 kg batches (Kulkarni *et al* 1980) lead to the important conclusion that the Kroll process is highly suitable for scaling up operations and the knowledge base generated will be adequate to design and engineer process equipment for much larger batch sizes.

3. DMRL technology for 2000 kg/batch sponge production

In the year 1985, the Defence Metallurgical Research Laboratory, Hyderabad, commissioned a Technology Demonstration Plant for titanium sponge production on 2000 kg per batch size by the Kroll process. The DMRL facility is equipped to study and establish the process parameters for (i) TiCl_4 purification by two-stage fractional distillation for the production of pure TiCl_4 at a rate of 150 kg/h, (ii) magnesiothermic reduction of TiCl_4 followed by vacuum distillation in two

factor (crucible) and its size reduction operations (Sridhar Rao and Subramanyam 1985; Subramanyam and Sridhar Rao 1986). Realizing the importance of recycling the by-product magnesium chloride for the economic production of titanium sponge, DMRL has parallelly progressed an R & D programme on the development of the fused-salt electrolytic process for regenerating magnesium and chlorine, in collaboration with the Central Electrochemical Research Institute, Karaikudi (CECRI).

Figure 1 depicts the DMRL flow sheet for titanium sponge production starting from raw titanium tetrachloride.

4. Chloride purification

A two-stage distillation scheme has been designed and set-up to separate (i) dissolved gases like O_2 , N_2 , Cl_2 , HCl , $COCl_2$, COS etc, (ii) volatile impurities like $SiCl_4$, $SnCl_4$, CCl_4 , S_2Cl_2 , CH_3Cl etc and (iii) other high boiling impurities such as $FeCl_3$, $NbCl_3$, $TaCl_5$, C_6Cl_6 , $TiOCl_2$ etc. The distillation columns are equipped with suitable heaters, sealless pumps, valves and instruments like level transmitters, diaphragm sealed pressure gauges, flow transmitters, etc. All the field instruments are interfaced with the process computer (DCS) and all the heaters are also connected to DCS through thyristor controllers.

The raw tetrachloride is purified in the first distillation column to separate dissolved gases and all low boiling impurities such as $SiCl_4$, $SnCl_4$ etc as per the typical operation conditions given in table 1 and distilled through the second stripper column to obtain pure $TiCl_4$ suitable for reduction.

5. Metal production – 2000 kg batches

The crucial step of sponge production is the reduction process operation and it involves careful control of process parameters viz. reaction temperature, pressure and $TiCl_4$ admission rate. Also, the scheme of $MgCl_2$ removal from the reactor during reaction, quantity of excess magnesium used and control of generation of titanium lower chlorides are other important aspects which can significantly influence the process operation. The quality of sponge is dependent on the reduction process parameters as well as subsequent vacuum distillation process parameters (temperature and duration) even if the input materials ($TiCl_4$ and Mg) are of high quality. In the DMRL facility 24 experimental production runs have been carried out and various process parameters of sponge production have been thoroughly studied (Subramanyam *et al* 1990). Typical process parameters found optimal are presented in table 2. Figure 2 is a 2000 kg sponge cake produced in one of the experimental runs. Table 3 presents typical analysis of titanium sponge produced in the facility.

6. Development of 4000 kg combined process technology

Combining the reduction and vacuum distillation processes to confine the two operations to a single station operation is a recent state-of-the-art technology and

is now widely used for large scale production of titanium sponge more economically. Decreased power consumption, increased equipment productivity, reduced labour requirement and increased quality of the product are the main advantages claimed by the combined process (Ikeshima 1985; Noda 1988; Ke and Huijuan 1989). In

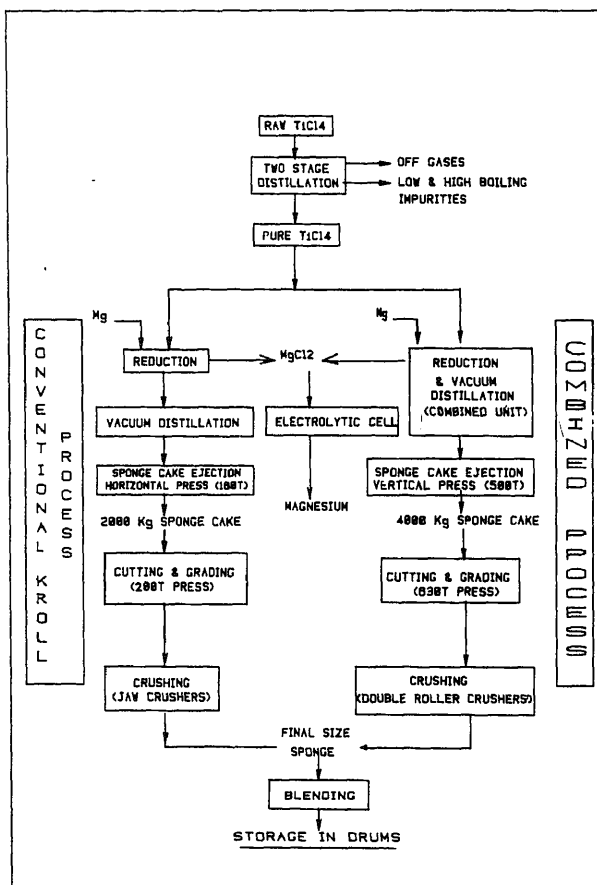


Figure 1. DMRL flow-sheet for the demonstration of titanium sponge production technology.

Table 1. Typical operating conditions of the distillation column.

Feed rate	160 kg/h
Distillate rate	5 kg/h
Reflux rate	40 kg/h
Bottom (product) rate	150–155 kg/h
Reflux ratio	8 : 1
Bottom temperature	138.1°C
Top temperature	136.5°C
Column pressure	1–2 psig
Sn level in bottom fraction	20–25 ppm
Sn level in top fraction	200–250 ppm

Table 2. Typical process parameters – 2000 kg/batch.

<i>Reduction</i>	
Excess magnesium	30–40%
Temperature	830–860°C
Reaction time	24 to 30 h
TiCl ₄ feed rate	300 kg/h (max)
No. of tappings of MgCl ₂	12–16
<i>Vacuum distillation</i>	
<i>Temperature</i>	<i>Soak time</i>
300°C	6 h
700°C	8–10 h
975°C	40–45 h
Ultimate vacuum	10 ⁻³ mm Hg (abs)

Table 3. Typical quality analysis of titanium sponge cake.

Location	Analysis (wt %)				Hardness (BHN)
	O ₂	N ₂	C	Fe	
Centre	0.0866	0.0012	0.0031	0.0140	90
Side	0.0878	0.0041	0.0226	0.0940	153
Bottom	0.1300	0.2000	0.0170	0.3000	213

the combined process, after the reduction operation the reaction mass is immediately subjected to vacuum distillation without involving intermediate cooling, opening of the reactor, reloading of the batch into the vacuum distillation unit and reheating of the mass. However, the crux of the technology lies in the design of the process equipment especially the heated interconnecting pipe (between the process reactor and the condenser reactor), the high temperature, high vacuum isolation valve and the top transfer system for tapping out periodically the by-product liquid magnesium chloride from the reactor.

Based on the experience gained in the operation of the 2,000 kg/batch equipment, DMRL is currently involved in the task of developing the combined process technology on 4000 kg/batch scale. Design of equipment and other related systems for this larger unit has been carried out in association with MECON and IGCAR for demonstrating this latest technology for its subsequent commercial implementation. All the equipment have now been installed and the reactor assembly is being subjected to pre-process testing.

Salient features (figure 1) of the DMRL combined process technology include the following: (i) operation of reduction and vacuum distillation processes using a single double purpose 480 kW pit type electric resistance furnace, (ii) a 150 mm dia. stainless steel interconnecting pipe encircled by specially designed electric heaters, with an isolation valve, to combine the two stainless steel reactors positioned side by side, (iii) a valveless top transfer system for tapping the by-product liquid magnesium chloride from the reactor during the reduction stage into a specially designed ladle by the application of pressure/vacuum, (iv) an insulated ladle that acts as a receptacle for liquid MgCl₂ which is essentially needed in an integrated plant for transferring the salt from the reactor to a fused salt electrolytic cell for



Figure 2. 2000 kg titanium sponge cake produced at DMRL.

the generation of magnesium and chlorine for recycling, (v) a sophisticated sponge cake ejection system and mechanical processing and comminution system and (vi) computer based instrumentation and process control of various process parameters.

7. Process equipment

7.1 Reactor assembly

Figure 3 is a schematic of the combined process equipment installed at DMRL. It comprises a set of two identical stainless steel reactors (1.5 m dia and 5 m high) coupled by an interconnecting pipe with a specially designed high temperature, high vacuum isolation valve. A 480 kW pit type electric resistance furnace provides

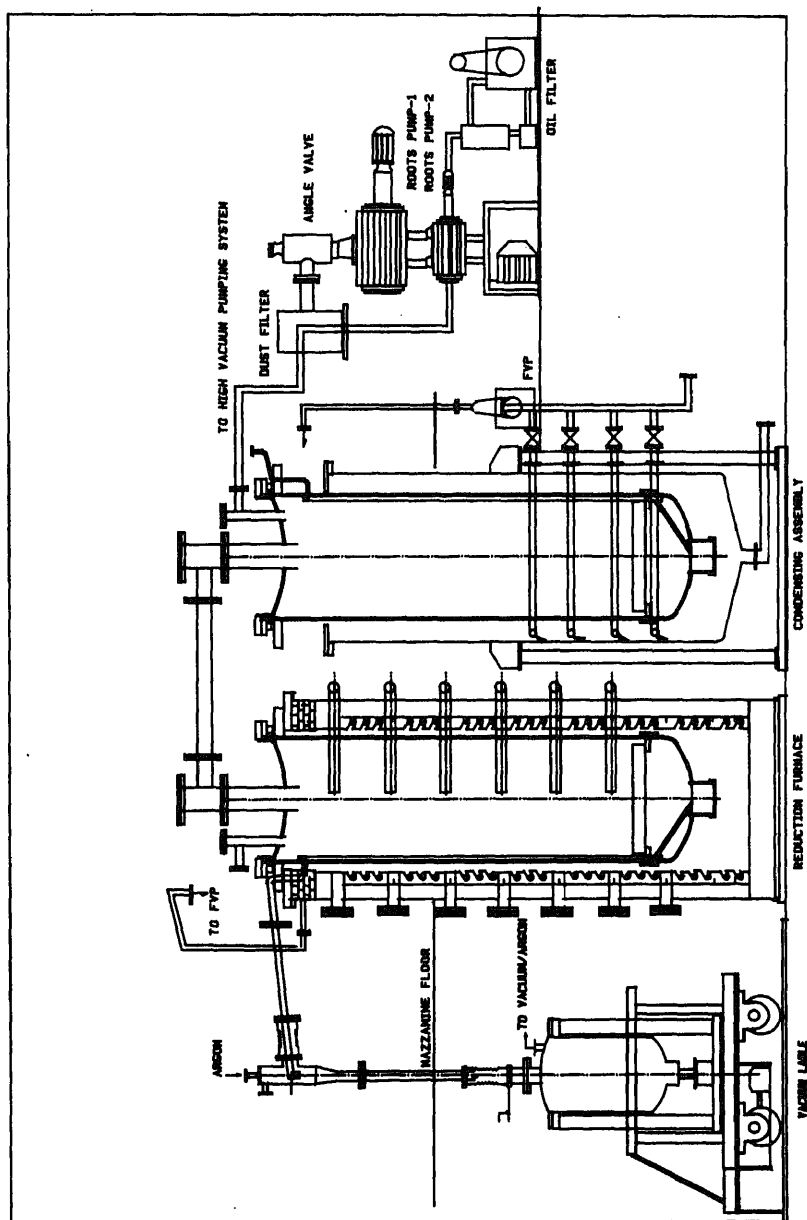


Figure 3. Combined Process equipment (4000 kg/batch - DNIRL).

the heat requirements for reduction and vacuum distillation operations. A condenser station with elaborate cooling arrangement will be in operation during the vacuum distillation process for receiving and condensing the excess magnesium and residual magnesium chloride in the second reactor.

7.2 $MgCl_2$ top transfer system

Figure 4 is a schematic of the top transfer system for the periodic withdrawal of molten $MgCl_2$ from the reactor. It comprises a semi-circular stainless steel pipe welded all along the height of the inner wall of the reactor through which molten salt can flow upwards from the bottom of the reactor to outside. At the exit point the liquid is directed through an inclined stainless steel pipe terminating in a surge vessel the bottom of which is connected to a vacuum ladle through a steel pipe. Tapping of $MgCl_2$ is achieved either by pressurization of the reactor or by applying vacuum on the ladle or by both these techniques if the situation so warrants. When tapping is not in progress the surge vessel is closed and a back pressure of argon is maintained to contain the by-product within the furnace zone of the reactor so as to eliminate the possibility of $MgCl_2$ rising into the cold zone of the tapping pipe.

7.3 Ladle

As shown in figure 4 the ladle is a cylindrical carbon steel crucible placed inside a larger cylindrical vessel with insulation in between. Necessary provisions for evacuation and pressurization for receiving the by-product and for teeming the same into trays have been made. Molten magnesium chloride enters into the ladle through a nozzle fitted to the top closure, which is in turn connected to the surge vessel through a stainless steel bellow. The ladle rests on three load cells so as to measure the quantity of salt received by it in a given tapping. In addition to load cells a level indicator which generates an electric signal to stop further flow of magnesium chloride automatically when the required quantity is tapped is also provided to ensure correct amount of tapping.

The ladle chamber is completely insulated such that molten material can be retained without solidification for about 3 h. An LPG burner initially heats up the chamber. The ladle can be moved on rails so as to take it to the salt bay for teeming into trays by pressure transfer. In an integrated Titanium Sponge Plant the molten magnesium chloride can be transferred directly into the electrolysis cells or a holding furnace.

As a prelude to the process operations, the top transfer system was subjected to a hot trial run. About 2000 kg of magnesium chloride was taken into the reactor, heated to a temperature of 800°C and transferred into ladle by applying pressure. The pressure requirement mainly depends on the liquid level inside the reactor and the desired rate of tapping. Temperature and pressure control, maintenance of slightly higher back pressure in the tapping line (as compared to the reactor inside pressure when tapping is not in progress), and automatic tapping of $MgCl_2$ using DCS have all been successfully demonstrated. The details of the top tapping experiment are given in table 4.

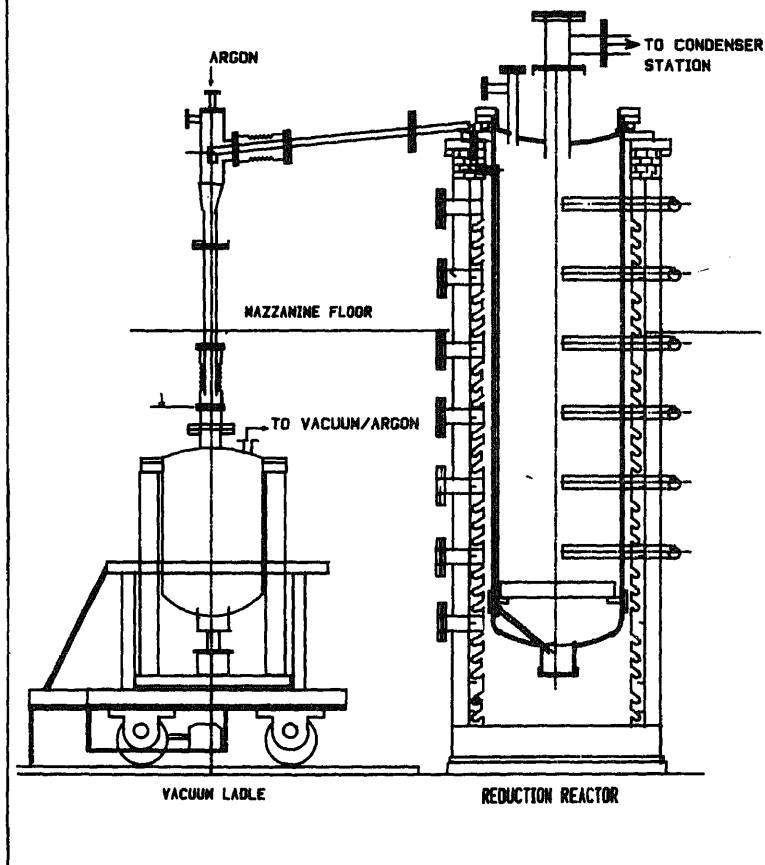


Figure 4. Top transfer system for magnesium chloride.

4.4 Process computer

A 16 loop Distributed Control System has been installed and put into operation for automatic control of the various process parameters of TiCl_4 purification and the combined unit. The DCS is also used for monitoring the process operations and logging the process data.

The process computer (DCS) with 16 main control loops, 16 auxiliary control loops and 512 digital I/Os is capable of handling 60 high level analog inputs directly connected to the system. Also 248 low level analog signals are connected to a serial port (RS-422 link) through an Analog Signal Multiplexer (ASM). The automatic control is accomplished with feed back on all process operations connected

Table 4. Details of experiment on top transfer of MgCl_2 .

Tap No.	Reactor pressure (psig)	Duration (sec)	Qty. of MgCl_2 tapped (kg)
1	8-9.6	50	345
2	8.2-9.9	65	460
3	8.5-10.1	90	633
4	8.5-11.1	70	642

to the DCS. The configuration and the user friendly software with complete failure feed back analysis was entirely developed in-house. On execution of some data acquisition program, the process computer provides a variety of process data which can be recorded using a printer at any selectable time interval.

7.5 High vacuum pumping system

The vacuum pumping system for carrying out vacuum distillation mainly consists of two high capacity roots pumps and an oil rotary vacuum pump connected in series with necessary valves and interlocks. A cryogenic cyclone separator and a cryogenic circulating type oil wet filter both operating at -10°C are installed ahead of the roots pumps for trapping all condensable vapours and carry over solid particles. The system is operated through a remotely located control panel with necessary interlocks, safety features and audio-visual alarms to indicate any malfunctions.

7.6 Sponge cake ejection press

A 500 T hydraulic vertical press (figure 5) is installed for ejecting the sponge cake from the reactor. With the help of a set of spacers the ram pushes the sponge cake into a steel container mounted vertically over the retort. The container is provided with necessary nozzles for evacuating and back filling with argon before ejecting the cake.

7.7 630 T guillotine press

First breakdown of the sponge cake will be carried out on a specially designed 630 T hydraulic guillotine press. The sponge cake is kept on the moving shuttle of the press and is supported by a set of V blocks. A long sharp edged hardened steel tool is used for skinning out the outer impurity rich layers of the cake as well as for cutting the sponge cake into smaller lumps of about 150 mm size. At this stage of operation, sponge is also graded into different fractions. The press has been commissioned and crushing and grading of sponge cakes of 2000 kg has been satisfactorily demonstrated.

7.8 Facilities for crushing and blending

A 200 T vertical press with a steel cutting tool is employed for cutting bigger

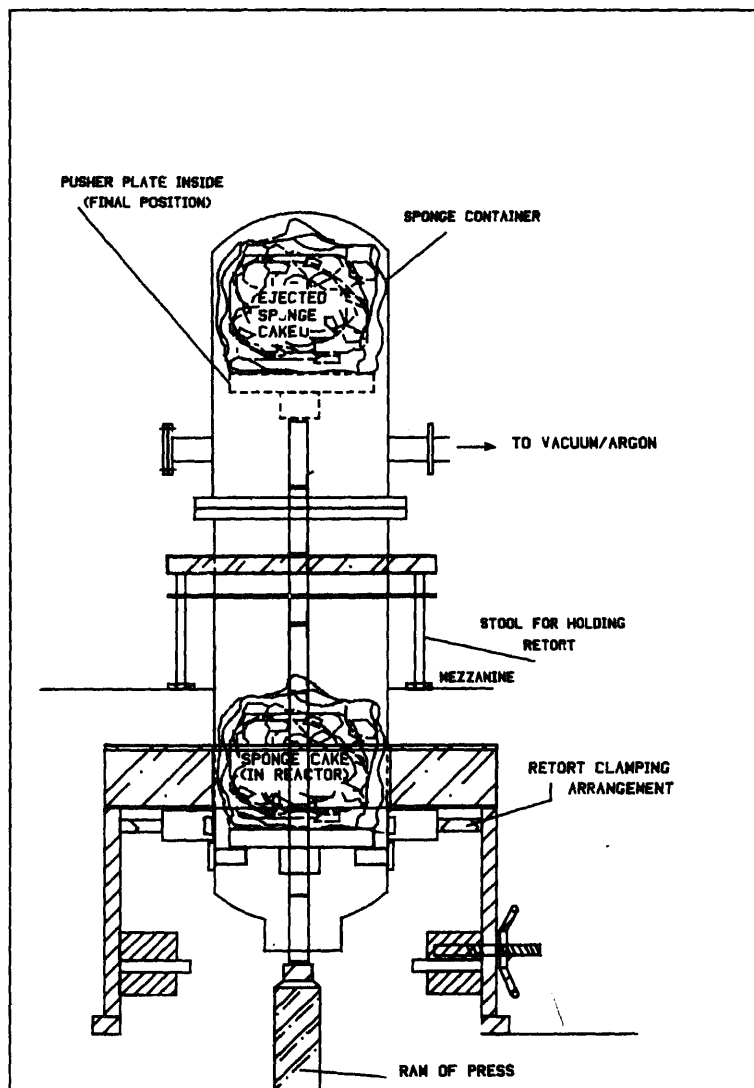


Figure 5. General arrangement of 500 T press with retort and sponge container.

sponge lumps to a size of about 150 mm which will then be subjected to primary crushing in a toothed type double roll crusher to a size of 75 mm. Secondary crushing will also be done in a second toothed type double roll crusher to a final size of -25 to $+2$ mm. A double cone blender of 1 T capacity is used for blending of sponge lumps to make a 'lot' of uniform quality.

Currently primary and secondary crushing of sponge is being carried out in jaw crushers. Use of jaw crushers for this purpose, however, has not been found to be efficient calling for repeated recycling. Compaction/flattening of sponge with rise in temperature is yet another problem frequently faced with jaw crushers. In the light of the experience gained and based on satisfactory trials conducted on roll crushers, two numbers of double roll toothed type roll crushers are under procurement.

8. Development of magnesium chloride technology

With a view to recycling the by-product anhydrous magnesium chloride, a 30 kA mono-polar modular type cell with 12 modules of 2.5 kA each has been designed, commissioned and successfully operating over prolonged periods (Nataraj Sekhar *et al* 1987). Based on this experience, a 7 kA, 2-module cell with 5 bipoles in each module has been designed and fabricated. Commissioning trails of the same are in progress.

9. Summary

The Technology Development Centre for titanium sponge production established at DMRL is a unique facility specifically designed to develop the Kroll process of titanium sponge production on a commercially viable scale. The intention is to develop and demonstrate the technology to prospective entrepreneurs on a full size unit so as to avoid the necessity of further scale up and its associated uncertainties. Commercial plants of any capacity can be set up by the installation of a plurality of the type of equipment set up and demonstrated at DMRL.

The above objective in respect of 2000 kg batch by the conventional two-step Kroll process has already been achieved. Substantial progress has also been made in the establishment and commissioning of the 4000 kg batch equipment of the combined process route. Top tapping of magnesium chloride into the vacuum ladle and teeming of the tapped out magnesium chloride from the ladle into trays using computer controlled instrumentation (a crucial and critical operation in sponge production by the combined process route) has recently been successfully demonstrated. Controlled cutting and grading of sponge cake on the 630 T capacity hydraulic guillotine press with specially designed tooling has also been demonstrated on a 2000 kg sponge cake. From the progress achieved, it is expected that the technology for titanium sponge production in 4000 kg batches by the combined process route will be demonstrated and optimized shortly. Parallely DMRL has worked out the cost estimates for establishing a 1000 TPY Integrated Titanium Sponge Plant with a matching Magnesium Plant for recycling by-product magnesium chloride based on the equipment designs evolved as described above.

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Technology Development for large scale titanium sponge production is a multi-disciplinary activity and active contributions of various agencies and individuals have been instrumental in the implementation of this programme.

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The design of the Kroll reactors and associated equipment have been evolved after extensive discussions with Shri S C Chetal and his team of Engineers from the Indira Gandhi Centre for Atomic Research, Kalpakkam (IGCAR) and Shri

M Seenaiiah, Nuclear Fuel Complex (NFC), Hyderabad. Stage-wise inspection of the reactor vessels during fabrication has been carried out by Shri R Madeswaran, IGCAR, strictly according to ASME Code for pressure vessels. Smt Uma Seshadri and her colleagues at IGCAR, Shri D Sreedhar, NFC and Shri G V S Brahmendra Kumar, DMRL were responsible for the design, erection, testing and commissioning of the computer based DDC system for the chloride purification and the Combined Process equipment. Field fabrication and commissioning of the various auxiliary units and electrics have been carried out by Messrs S A Jesudasan, R Guruprasad, S N Narendra Babu and M Kirtania, DMRL and Mr Johnson D'Souza, NFC. The outstanding contributions and the dedicated efforts put in by all the above Scientists and Engineers from IGCAR, NFC and DMRL are gratefully acknowledged.

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Technology development and applications of composites at HAL

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Abstract. Composite materials for aerospace applications through in-house R & D and through collaboration with overseas aerospace organizations and National Laboratories covering a wide spectrum including glass/carbon/kevlar fibre reinforced plastics, metal and Nomex honeycomb sandwich structures, laminated composites, metal matrix composites and metallo-ceramic composites.

Keywords. Polymer composites; honeycomb sandwich structures; metal matrix composites; glass/carbon/kevlar fibre reinforced plastics; metallo-ceramic composites.

1. Introduction

Composites are taking an important place in the manufacture of civil and military aircraft as they provide unique design opportunities to suit specific applications. Composite materials offer specific property advantages like higher modulus per unit weight (specific modulus) and higher strength per unit weight (specific strength), resistance to fatigue and corrosion, better thermal expansion characteristics and conductivity (for MMC) damping property and design flexibility. Research and development at HAL, in five distinct areas, namely polymer composites, sandwich structures, metal matrix composites, high temperature metal ceramic composite coatings and metallo-ceramic brake materials have led to the application of composite technology to specific areas in the manufacture of advanced aircraft, helicopters and jet engines.

R & D in fibre reinforced plastics (FRP) started in the seventies for non-structural GFRP fairing for Cheetah and Chetak helicopters, has matured into a well established technology with production facilities for manufacture of primary load carrying structural parts using carbon, kevlar and glass fibre composites and also hybrid composites to make 'engineered composites components' to meet varied properties in different regions of the same part. Design and development of foam or metal/plastic honeycomb core sandwich structures has been an important activity in HAL. Several process technologies in this field and optimization studies have been made and production facilities established with capabilities to manufacture primary structures such as, floor boards for helicopters, aircraft and space vehicles and complex shaped and curved structures such as wing flaps, tail plane structures, side panel for fuselage and cockpit structures for helicopters. A related area of work is the development and application of bonded laminated structures.

R & D in metal matrix composites taken up at HAL has been mainly in the areas of aluminium alloy-SiC and magnesium alloy-SiC composites for structural applications. Metallo-ceramic composites and resin-fibre-ceramic composites have been developed as friction material for aircraft brakes. Another area of research at

HAL in this field is the metallo-ceramic composite coatings on surface of jet engine components to protect against high temperature erosion and water. A number of such coatings have been established using electrochemical deposition, plasma coating and diamond jet coating techniques. Table 1 summarizes the development and application of composites in aircraft/helicopters and engines manufactured by HAL.

2. Preliminary studies

At HAL, preliminary studies on composites started in 1971 with the licensed manufacture of Cheetah and Chetak helicopters. The R & D consisted of developing silane treated woven glass cloth to specifications, selection of polyester/epoxy resins, establishing process technology, testing and certification for airworthiness. The effect

Table 1. Composites in aircraft structures manufactured in India.

Glass fibre reinforced plastics	Chetak Helicopter - Fuselage fairings, doors Ajeet Aircraft - Nose cone, fairings, electrical boxes, fin tip Jaguar Aircraft - Wing leading edge, fin tip, Alpha boxes MiG Aircraft - Nose cone, fairings ALH Helicopter - Several structures and fairings
Foam and honeycomb sandwich structures	Cheetah and Chetak Helicopters - Floor boards ALH - Fuselage structures Jaguar - Front and fuselage structures, rudder, tail plane, flaps and undercarriage doors LCA - Front and fuselage structures, control surfaces and undercarriage doors (proposed)
Durestos-asbestos reinforced plastic	Jaguar - Drop tanks MiG - (proposed)
Carbon fibre reinforced plastics (CFRP)	ALH - Rotor blades, front fuselage and centre fuselage structures MiG - Fin tip, panels LCA - Wings, undercarriage doors (proposed)
Kevlar FRP	ALH - Cockpit structure, inspection doors, centre fuselage structures Dornier-228 - Several secondary items
GFRP/CFRP/Kevlar hybrids FRP	ALH - Rotor blade, flex beam LCA - Undercarriage doors (proposed)
Laminated composites	ALH - Elastomeric bearings
Aluminium SiC composites	LCA and undercarriage doors - (proposed)
Metallo-ceramic composites	Kiran, Avro, MiG, AN-32 Jaguar, Dornier, Cheetah/Chetak helicopters
Resin-fibre-ceramic composites	HPT-32 Piston engine trainer aircraft
Carbon-carbon composites	LCA, MiG, ALH: Brakes (proposed)
Super alloy-ceramic/metal carbide composite coatings	For surface protection of engine components

} Brake pads
(friction material)

f treatment of glass cloth, plasticizing of resin, curing cycles etc. on properties such as strength, rigid polyurethane foam and type certification for adding rigidity to FRP structures were part of these early studies. These resulted in the establishment of a full fledged GFRP shop at HAL for making non-structural GFRP fairings for helicopter body, door and polyurethane foam filled sandwich structures including bonded rotor blades (figure 1).

More recent work

With the induction of the Jaguar aircraft into the defense services, HAL acquired several new technologies and augmented existing ones to cope with the steep advances in high technology areas. One significant technology is the honeycomb bonding and metal-to-metal adhesive bonding which led to series production of about eighty different varieties of honeycomb assemblies (figure 2). A few examples of technology development/improvements undertaken during this phase are given below.

1 Honeycomb machining

Technology for machining of complex shapes with curved surfaces have been established. Computer programmes for 5 Axis CNC machining for various shapes

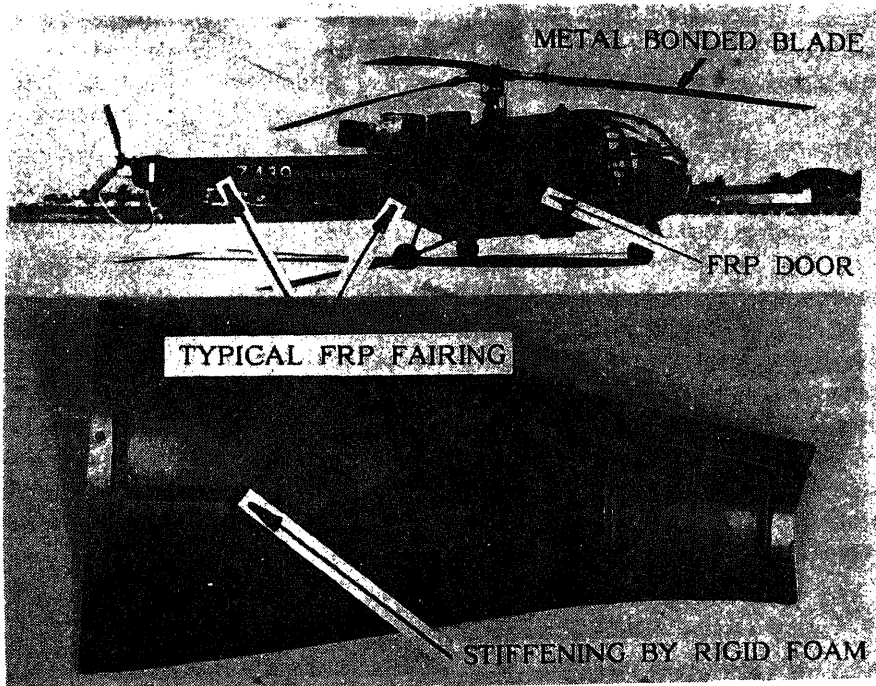


Figure 1. FRP applications in Chetak helicopter.

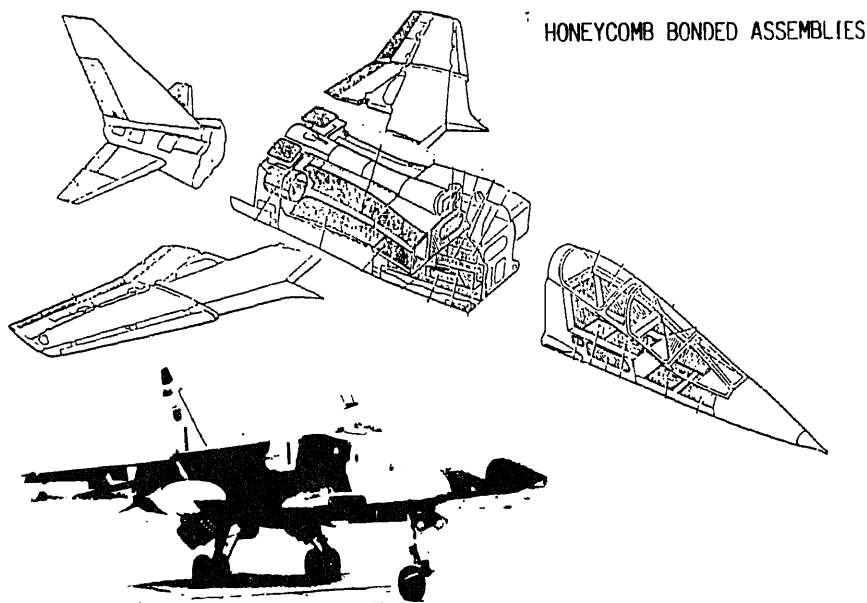


Figure 2. A view of honeycomb bonded structures in Jaguar.

have been developed. Vacuum application techniques for holding the work piece on to the machine bed and the development of suitable vacuum fixtures are important aspects of this technology development (figure 3). Cost effective techniques for machining of flat surfaces of soft cores such as plastic foams and honeycombs were developed along with the machinery and equipments indigenously. Also, for edge crushing and edge preparations. Honeycomb core crushing equipment and the technology were simultaneously developed (figure 4).

3.2 *Effect of surface preparation on the bonding strength*

Another area where technology improvements in bonding is carried out is in the optimum surface preparation of the metal/composite interface. Bonding surface is a very important area which controls the bond integrity. Surfaces with blasted, epoxy coated, pickled, anodized and epoxy spray were generated and experiments were carried out by bonding these surfaces with glass fibre, carbon and asbestos composites. Tensile lap shear specimens were made and tested for shear. Optimum surface preparations for each type of composites were developed. For carbon fibre composites ideal surface is anodized and epoxy primer coated; and for asbestos prepregs anodized surface gives excellent results.

3.3 *Floor boards and complex shaped sandwich structures*

Adopting the honeycomb bonding and composites technology concepts to other projects, several developments have been carried out. These include development

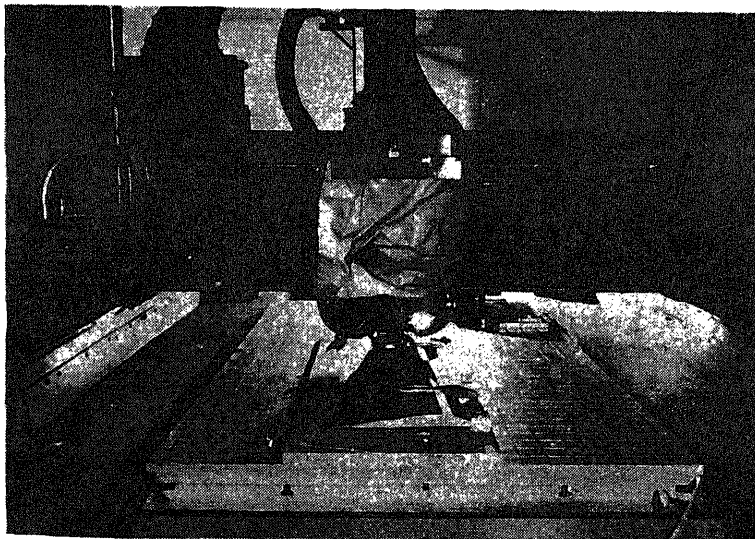


Figure 3. Five-axis CNC honeycomb core carver.

of honeycomb floor board for Chetak/Cheetah helicopters. ASLV and PSLV structures and now for the light helicopters. For curved shapes such as wing flaps, radars, side panels, etc., bonding technique for skin to core, vacuum bagging, prebonding and postbonding inspection techniques have been developed. Another significant development is paratrooper seat which consisted of a back rest made out of a carbon fibre composite box skin and a seat pan made out of carbon fibre skin and metal honeycomb core. In the development of various types of floor boards, the technologies of insitu bonding of locating points and load carrying members and also post bonding techniques for assemblies have been perfected. A typical honeycomb floor board and a fully assembled paratrooper seat are shown in figure 5.

3.4 *Radome structures*

Development of radome structures involved optimization of the skin and core thicknesses and bonding techniques to achieve the required electro-magnetic transparency. Technology for shaping and hot forming of non metallic honeycomb core "Nomex" was developed successfully to make sandwich structures for radomes. A large composite radome of diameter 7,300 mm was recently fabricated in HAL which is the largest composite structure produced in this country using glass impregnated advanced composites. Figure 6 gives some illustrations.

3.5 *Defect identification and characterization*

A number of test panels were fabricated using carbon fibre composites with various induced defects such as debonds, delamination and foreign object damages (FODs). Both straight and stepped panels were fabricated. The panels were subjected to

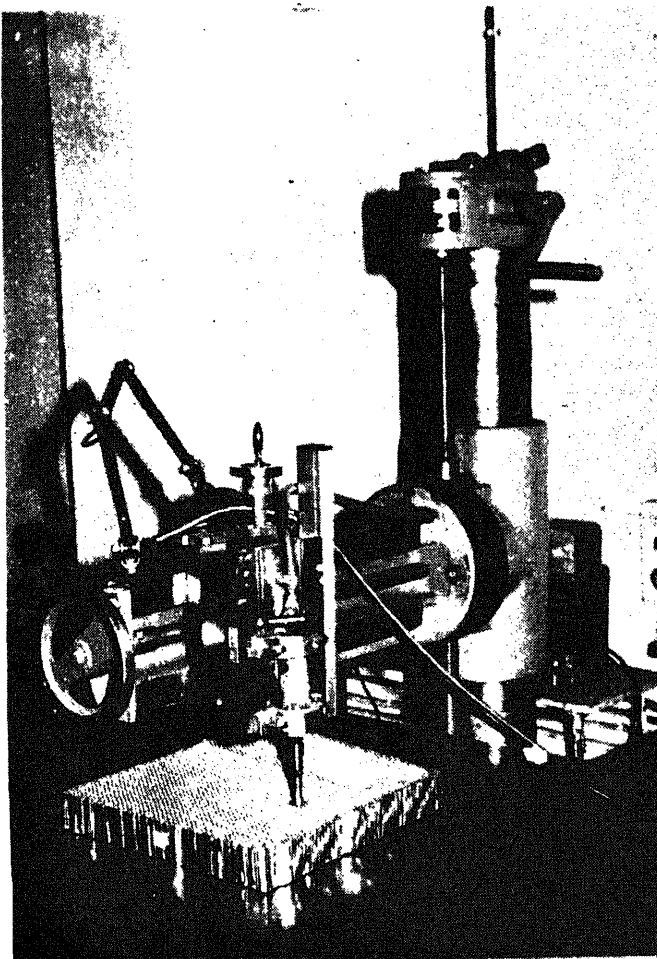


Figure 4. Honeycomb core machining equipment for flat surface machining.

inspection by NDT techniques, namely, ultrasonics (through transmission ultrasonic C-scan and contact methods) and low energy X-ray radiography. C-scan revealed debond conditions induced by vidax and teflon but failed to detect the other defects namely non-metallic net and aluminium foil. Contact method showed varying levels of signal amplitudes, characteristic of each induced defect. Low energy X-ray radiography revealed all the defects except the defect induced by vidax. A combination of ultrasonics and X-ray radiography can identify all possible defects that may occur in a composite component. Also it is possible to characterize the defects using through transmission ultrasonics (figure 7). Improved methods of identification of defects using C-scan multi-colour ultrasonic technique are also available. Based on the technology, a large ultrasonic C-scan has been designed and is under fabrication jointly by Aeronautical Development Agency, Hindustan Aeronautics Centre for Artificial Intelligence and Robotics and Vivace Sonics.

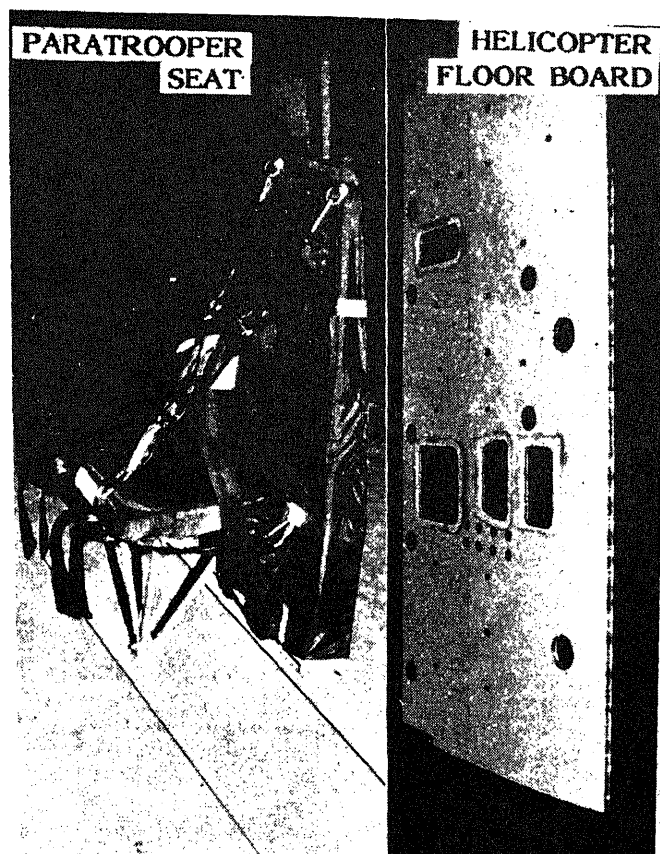


Figure 5. A typical floor board for helicopter applications and a paratrooper seat assembly for Dornier aircraft made from composites.

3.6 Resin injection moulding

Technology was developed for moulding fibre reinforced plastic components by injection moulding. Glass fibre cloth stitched to the shape required is inserted in the predesigned mould and resin is injected under pressure (figure 8). A large number of components have been produced for domestic and for export market.

3.7 FRP pipes

A unique technology for making complex shaped pipes in reinforced plastics has been developed by adopting the investment casting technique from the Foundry industry. Wax patterns are made and resin impregnated tapes are wound to build adequate thickness. After room temperature curing, the wax is melted out at 80°C in an oven followed by a post curing cycle at an elevated temperature. Production facilities have been established both for Indian and for export market (see figure 9).

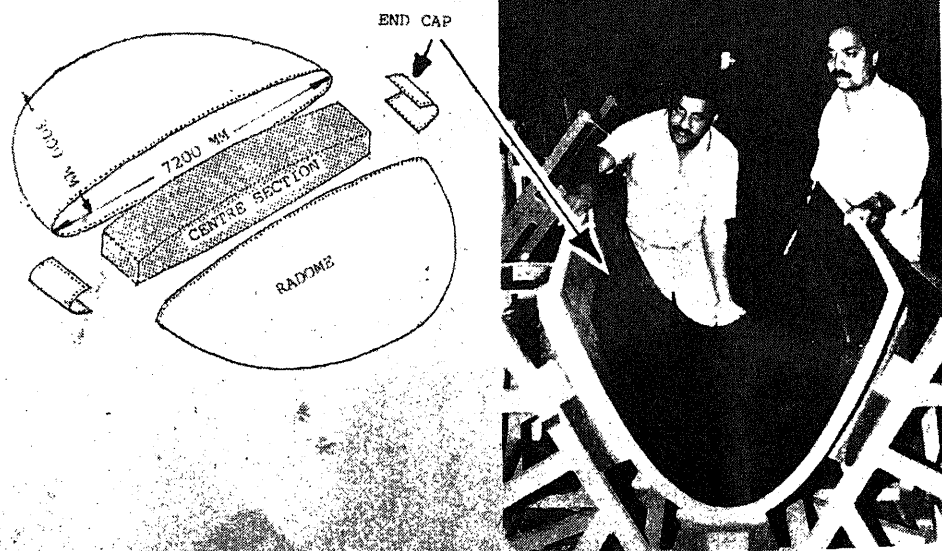


Figure 6. A schematic view of the complete arrangement of the composite radomes and a view of the end cap.

4. Composites for advanced light helicopter and light combat aircraft

The Advanced Light Helicopter (ALH) and Light Combat Aircraft (LCA) make extensive use of composites (figures 10 and 11). Carbon, kevlar, glass reinforced plastics and their hybrids as well as metal and nomex, honeycomb sandwich structures are extensively used. An example of excellence in this field is the single piece moulded cockpit structure (carbon/kevlar) for ALH (figure 12). The main rotor blade for ALH is an illustration of the maturity in the design, development and manufacture of a composite of composites (figure 13). The honeycomb core and glass/carbon fibre skin for the blade aerofoil give desired strength and rigidity, the quantum and orientation of fibres give required directional property and fatigue resistance; and the flex collar provide adequate flexibility (by hybridization to take care of lead/lag/flap and torsion and meet the design requirement of hingeless rotor). LCA envisages utilisation of several advanced composite structures, the most significant among them being the carbon fibre composite wing under development by a national team of designers, scientists and technologists from HAL, ADA and NAL.

An important development in making these components has been the development of composite tooling itself. Tools are developed through master model techniques using glass, carbon, epoxy and wet layup techniques. These are initially cured under room temperature and then post-cured at elevated temperature to avoid

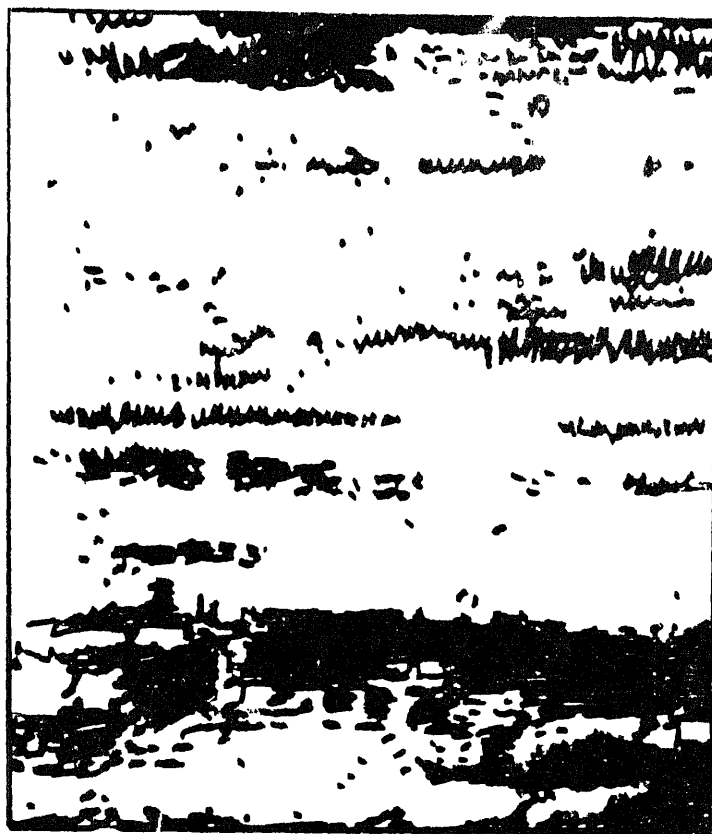


Figure 7. A C-scan ultrasonic plot showing the bonding integrity variations. Blank shows maximum integrity and dark areas show medium integrity.

varpage and for increased strength. Composite tooling technology apart from giving more dimensional accuracy is also a cost effective solution as otherwise these large complex tools would have required 5 axis CNC machining for metal moulds.

Plywood is perhaps the earliest example of laminated structures used in some of the older generation of aircraft. More advanced laminated composites are emerging with the advancement in bonding technology and high strength adhesives. It is proposed to use some of these for specific application in LCA and ALH and research and development has been taken up in some areas. High strength aluminium alloy thin sheet and carbon/kevlar/glass fibre reinforced plastic laminated structures for structural applications is one area of work. Metal/rubber laminated structures for elastomeric bearings is another area.

4. Metal matrix composites

A number of compositions of aluminium alloy 6061 and alloy 7010 with varying percentage of SiC particulates have been prepared and evaluated providing a range

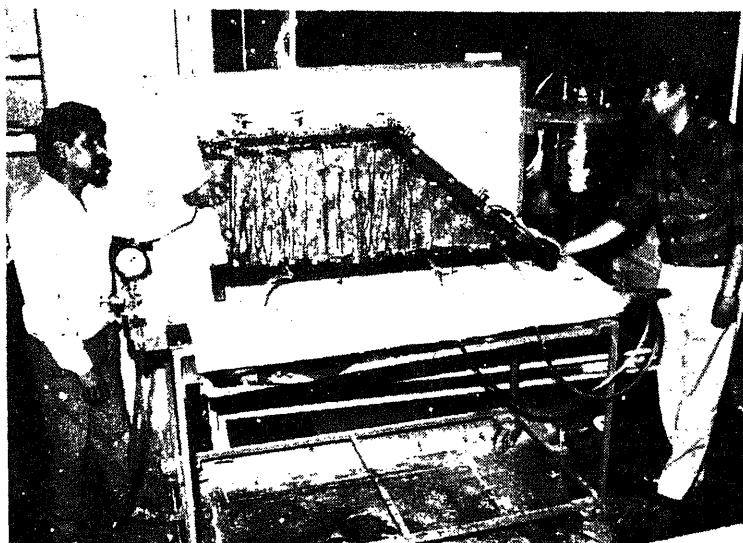


Figure 8. Resin injection moulding along with mould set-up.

of high strength and high modulus composites. MMC of this type have been produced both by foundry technique and powder metallurgy followed by consolidation through forging/extrusion. Technology has been established and hot press billets up to 150 mm dia. and extrusions up to 60 mm dia. have been made. Typical products planned are, aircraft forgings, low thermal expansion missile components, high modulus space vehicle components, etc. Shaped extrusions including tubes have been prepared in collaboration with National Physical Laboratory, Materials Division and Regional Research Laboratory, Trivandrum (figure 14). Recently the work on magnesium SiC composites using foundry route has also been taken up.

6. Metallo-ceramic and resin-fibre-ceramic composite brake material

Aircraft brake materials are essentially resin, copper or iron based with various other metallic, non-metallic and ceramic ingredients to provide a combination of a variety of properties required for aircraft brakes. Carbon-carbon fibre composite is the most recent and advanced brake material. When an aircraft lands and progressively comes to a halt, the kinetic energy is converted into heat energy by friction by the rubbing of surfaces of the brake material. Hence the brake material should have high friction coefficient and at the same time good wear resistance. The heat generated has to be dissipated and, therefore, it should have good thermal conductivity besides high specific heat to reduce rise in temperature. It should also have anti-seizure properties and high temperature strength and hardness. Design and development starts with an analysis of the braking requirements, namely the energy to be absorbed and the heat generated, based on which specific values are derived for coefficient of friction, thermal conductivity, acceptable wear, anti-seizure property and high temperature strength and hardness etc. Composition of the composite is



Figure 9. Complex composite pipes made out of GRP by wax investment process.

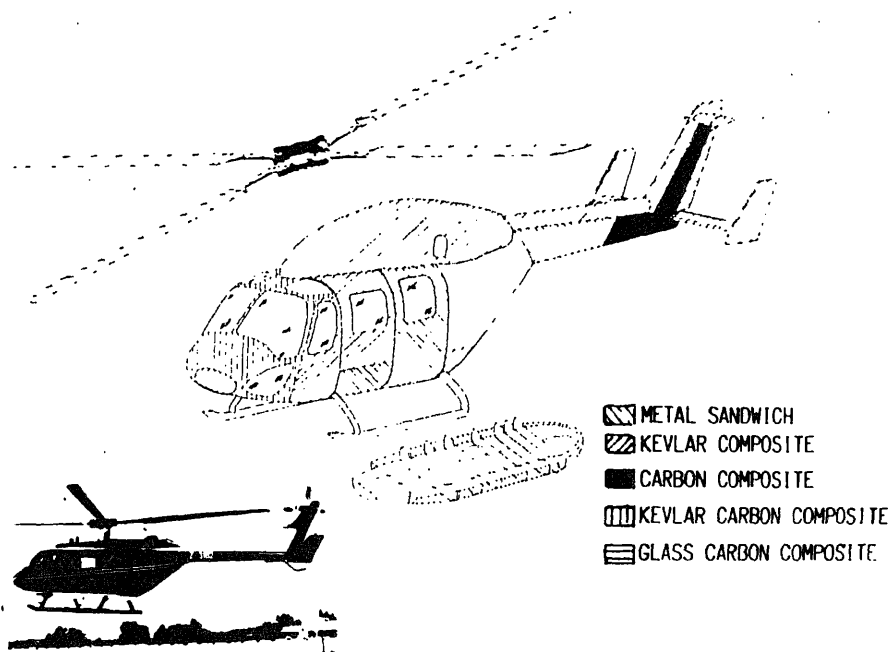


Figure 10. Advanced light helicopter and major areas where composites are made use of.

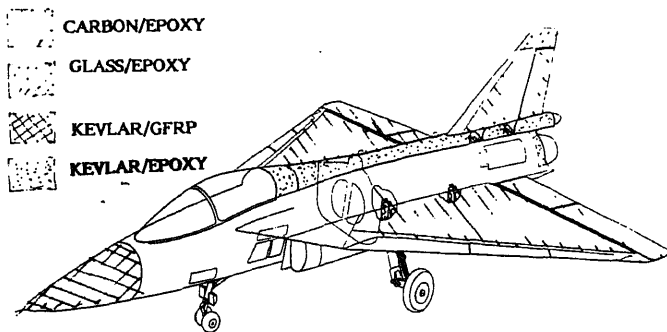


Figure 11. Light combat aircraft. Composite materials used on the aircraft are highlighted.

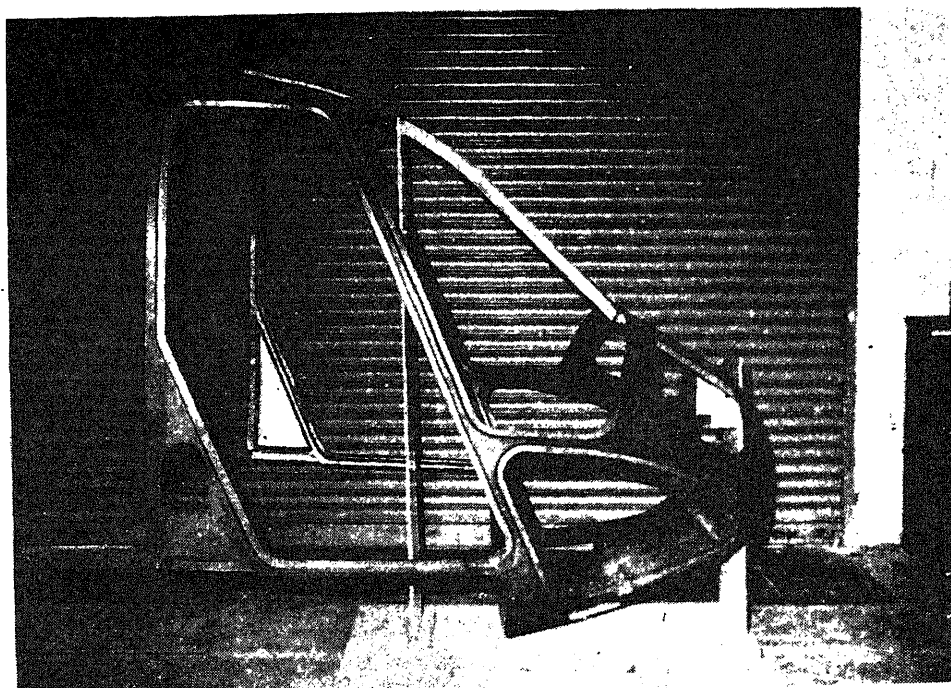


Figure 12. Cockpit structure for ALH-single piece composite component.

then selected based on statistically designed experiments to optimise composition and process parameters to meet these property requirements. The process route followed for a typical metallo-ceramic brake pad is shown in figure 15. For resin based brake pads low energy brake application used in piston engine aircraft, the process followed is by mixing the ingredients with resin and casting the resin to shape followed by finishing with machining and grinding operation. Working in close co-operation with Defence Metallurgical Research Laboratory, Hyderabad, and

COMPOSITE ROTOR BLADE

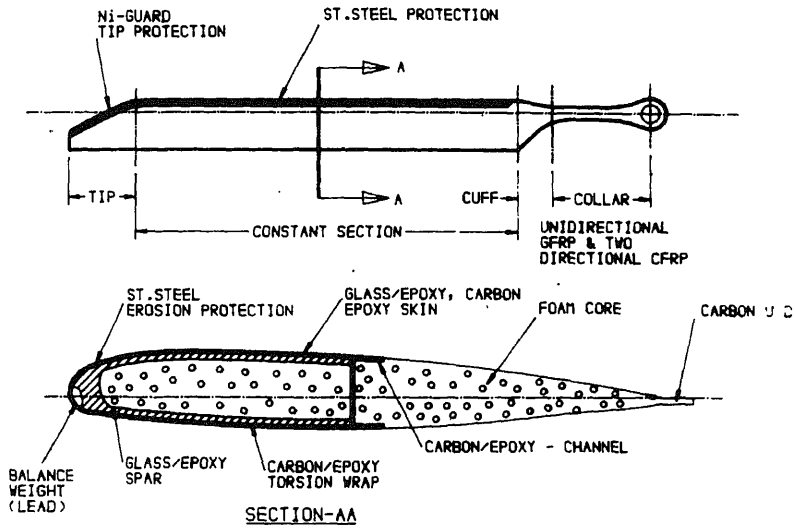


Figure 13. Composite main rotor blade and its section for an advanced helicopter.

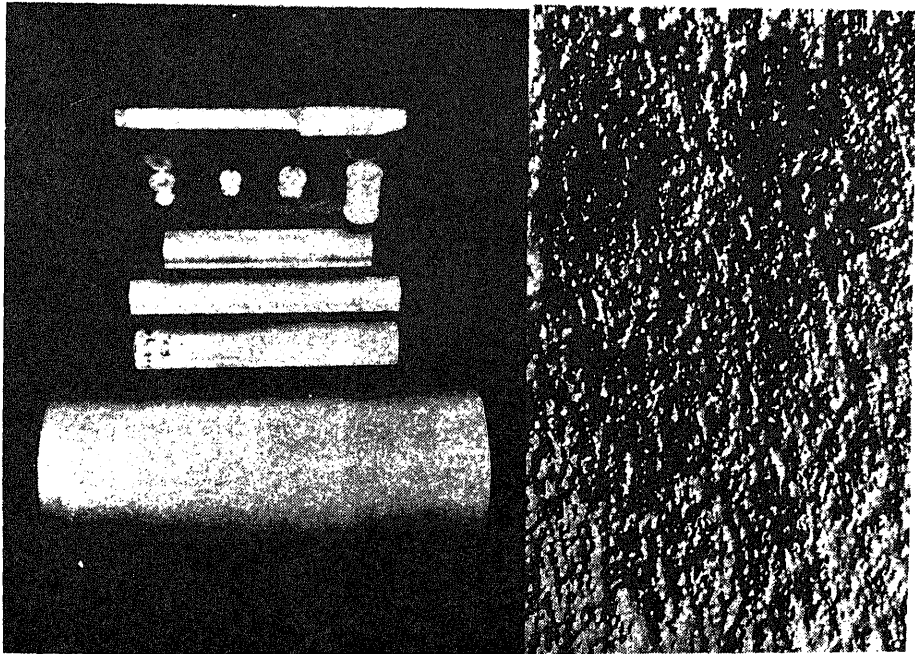


Figure 14. Metal matrix composites developed in-house. Typical microstructure is also shown.

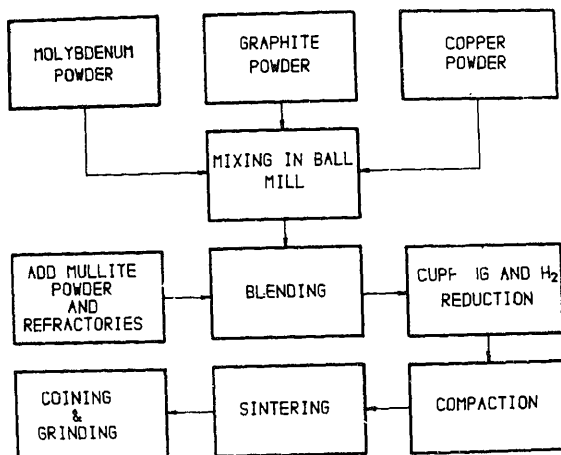


Figure 15. P/M process for manufacture of copper based brake pad segments.

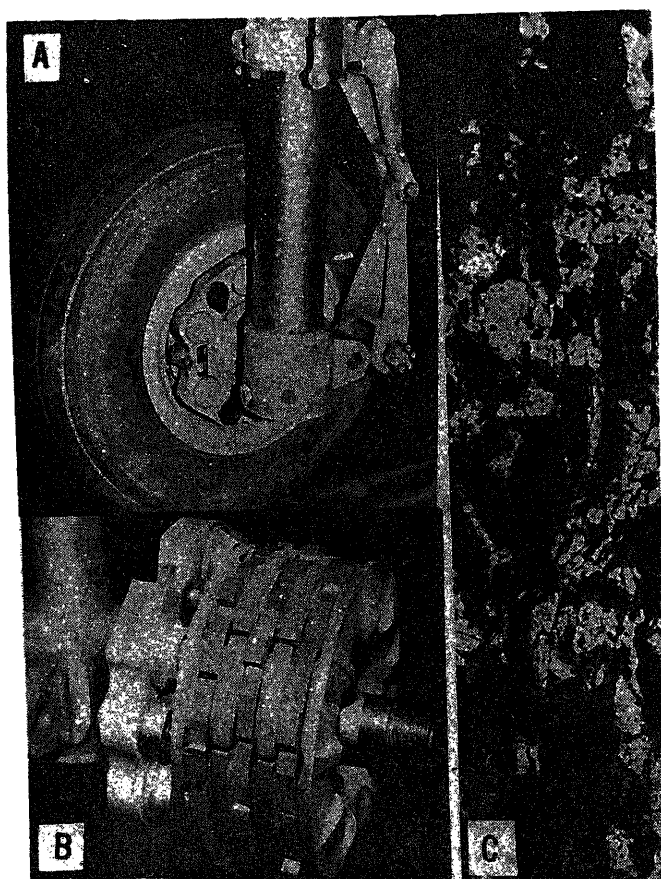


Figure 16. Brake pad development for a fighter aircraft landing gear. (A) landing gear assembly, (B) brake pad assembly and (C) a typical microstructure.

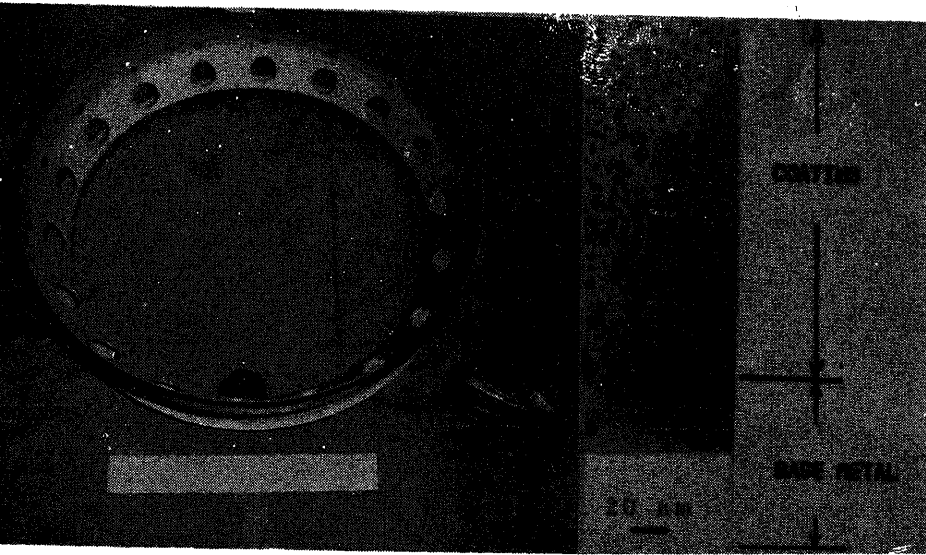


Figure 17. Jet engine components requiring cobalt chromium coating. Microstructure of the coating shown on right.

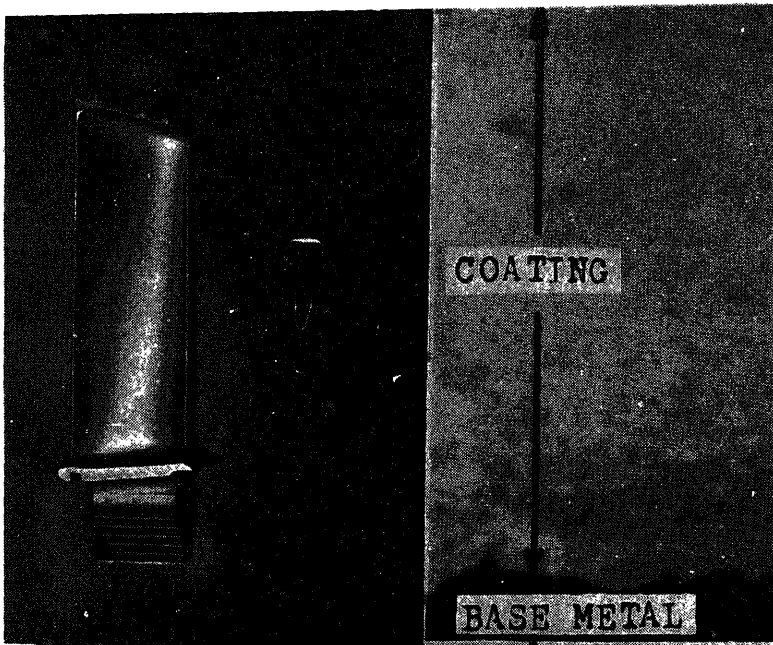


Figure 18. Jet engine turbine blade with chromium carbide coating. Microstructure of the coating shown on right.

IIT, Madras, HAL has developed and established technology for various types of aircraft brakes required for the military/cargo/passenger aircraft. Figure 16 shows a typical example.

7. Metallo-ceramic composite coatings

In order to increase the life of critical engine components for high performance jet engines, it is necessary to engineer the surface of the parts to provide high temperature corrosion and wear resistance. Metallo-ceramic composites using super alloys as matrix material are essentially employed as excellent coatings for this purpose. Several such composite coatings have been developed using plasma, Detonation gun (D-gun), electroplating and diamond jet techniques. Cobalt-chromium carbide composite is one such coating which is extensively used for hot end components of jet engines. Research and development was taken up to develop a process of co-deposition of cobalt and chromium carbide on to components. This has been successfully accomplished and production facilities are established. The essence of the technology development consists of designing a plating equipment incorporating an oscillatory perforated plate agitator to keep the fine chromium carbide particles in suspension so that they will be picked up along with cobalt ions and deposited during the electroplating process. A series of carefully planned experiments optimize the design for the same. A few examples of components and microstructure are shown in figure 17. Another example is a composite coating consisting of 75% chromium carbide + 25% nickel-chromium developed for use on Adour engine low pressure turbine blades (figure 18). In this case, the coating was deposited using a D-gun available at the Advanced Research Centre for Power Metallurgy, Defence Metallurgical Research Laboratory, Hyderabad. R & D using diamond jet coating techniques is also in progress for metal ceramic coatings.

8. Conclusions

Hindustan Aeronautics Limited has established a sound technology base and production facilities for composite materials for aerospace applications through in-house research and development and through collaboration with overseas aerospace organisations and national laboratories. The range of expertise and products cover a wide spectrum including glass/carbon/kevlar fibre reinforced plastics, metal and nomex honeycomb sandwich structures, laminated composites, metal matrix composites and metal-ceramic composites for aerospace structures, aircraft brake materials and for coating of jet engine components.

FOREWORD

This special issue of the Bulletin of Materials Science carries the Proceedings of the Fifth Annual General Meeting of the Materials Research Society of India, held at the Research Centre Imarat, Hyderabad from February 7 to 9, 1994. In his MRSI Honour Lecture Prof. M S Valiathan spoke about "Heparin bonding: Then and now" and touched on several fascinating issues such as materials and blood compatibility, heart-lung bypass systems, oxygenators and the artificial heart valve. A bright chapter in biomaterials in India was unfolded by the Lecturer at this meeting. The twelve Medal Lectures featured in this issue, cover a wide variety of topics such as characterization techniques, crystal growth, semiconductor films, magnetoelectric interactions, superconducting materials, surfactant materials, polymers, biomaterials, corrosion protection, creep and development of aluminium-lithium alloys. They make a strong impression of the high quality of current materials research concerns in Indian laboratories. Six lectures by overseas speakers provided an international perspective to the meeting.

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*The 1994 Distinguished
Materials Scientist Lecture*

*The Materials Research Society
of India*

Heparin bonding: Then and now*

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*Distinguished Materials Scientist Award Lecture presented at the MRSI Meeting, Hyderabad on February 9, 1994.

Born in 1934 in Kerala, M S Valiathan graduated from the Trivandrum Medical College in 1956. He received his postgraduate surgical training in the University of Liverpool Hospitals and became a Fellow of the Royal Colleges of Surgeons of England and Edinburgh in 1960 and a Master of Surgery from the University of Liverpool two years later.

After serving on the faculty of the Postgraduate Medical Institute, Chandigarh, Valiathan specialized in cardiac surgery at the Johns Hopkins and Georgetown University Hospitals in the United States and received the Fellowship of the Canadian Royal College in cardiovascular and thoracic surgery. Prior to his appointment as Professor of Cardiac Surgery and Director of the Sree Chitra Tirunal Medical Centre in 1974, he served as a visiting professor in biomedical engineering at the Indian Institute of Technology, Madras. Valiathan's work has been mainly in the field of cardiac surgery which he organized and brought to high professional standards at the Sree Chitra Tirunal Institute. Apart from the major commitment to cardiac surgery, he and his team carried out original studies on a tropical cardiomyopathy—endomyocardial fibrosis—and pioneered the concept of its geochemical aetiology. His other interest has been the development of biomaterials and medical devices and the promotion of a medical devices industry in the country. He has published a book and over 100 papers relating to cardiac surgery, endomyocardial fibrosis and biomaterials and contributed chapters to several books.

1200 M B Valiathan

He is the recipient of many honours for his scientific and professional work, including the Hunterian Professorship of the Royal College of Surgeons of England; Fellowships of the American College of Cardiology, National Academy of Medical Sciences, Indian Academy of Sciences, Indian National Science Academy, National Academy of Sciences, and Indian National Academy of Engineering; Kerala State Award in Science and Technology; R D Birla National Award in Medical Sciences; Om Prakash Bhasin National Award in Medical Sciences; Dhanwantari Prize of the Indian National Science Academy; Basanti Devi Amir Chand Prize of the Indian Council of Medical Research; and the Padma Bhushan. He served as a member of the Science Advisory Committee to the Indian Cabinet and as the President of the Association of Indian Universities. He is an honorary consultant in cardiac surgery to the Armed Forces.

It was under Valiathan's leadership that the Sree Chitra Tirunal Medical Centre made rapid strides and became an institute of national importance which is unique for the convergence of medical science and technology in its programmes. This novel approach to medical technology has yielded products for patient care such as the blood bag, oxygenator, hydrocephalus shunt, vascular graft and a tilting disc heart valve, and triggered the growth of a medical devices industry in India. After 20 years at Sree Chitra, Valiathan joined the Manipal Academy of Higher Education as Vice-Chancellor in 1994.

Abstract. Blood remains fluid so long as it flows in the cardiovascular system; it clots in other situations. While this phenomenon, vascular homeostasis, has been studied for a century, the development of artificial surfaces that induce minimal or no clotting became important only with the growth of cardiovascular surgery. The advent of the graphite-benzal konium-heparin surface which employed the ionic bonding of heparin was a milestone in the effort to develop non-clotting surfaces. The technique of ionic bonding was followed over the years by the grafting of heparin molecule to surfaces and most recently, by the covalent bonding of heparin. The covalent bonding of heparin preserves the non-clotting property of prosthetic surfaces for long periods and holds promise for numerous applications in cardiovascular surgery and other branches of medicine. The introduction of covalent bonding and similar approaches will greatly improve the biocompatibility and durability of the present generation of biomedical devices.

Keywords. Heparin bonding; graphite-benzal konium; blood compatibility; Carmeda surface.

1. A personal apologia

I would like to begin by expressing my gratefulness to the Materials Research Society of India for choosing me as the Distinguished Materials Scientist for 1993. It is a great honour which I shall cherish as a surgeon whose professional work was intertwined with that of materials scientists for many years. It is no less appropriate on this occasion to acknowledge the debt of surgery to materials science for the gift of innumerable devices which have lightened the burden of human suffering.

One is often told that surgery and scientific research are incompatible; that handcraft and brainwork are inharmonious. It is even alleged that excellence in one must exclude quality in the other. The antiquity of this fallacy—for that is what it is—is borne out by a voice from the past: 'The last part of surgery, namely operations, constitutes a reflection on the healing art. It is a tacit admission of the inadequacy of surgery. It is like an armed savage trying to get by force what a civilised man would get by stratagem'. That was John Hunter, the father of scientific surgery, speaking to us from the 18th century. As a surgical neophyte in 1960, I was therefore in illustrious company for seeking a role for research in surgery and regarding a surgeon as an investigator *par excellence*.

I undertook experimental studies for the first time on the problem of cirrhotic ascites in Dr Gibbon's laboratory in Philadelphia more than 30 years ago when portal hypertension and its complications loomed large in general surgery (Lalonde

et al 1964). I liked the philosophy and method of experiment and learnt to appreciate Claude Bernard's profound statement, 'In the search for truth by the experimental method, feeling always takes the lead: it begets the a priori idea or intuition; reasoning develops the idea and deduces its logical consequences. But if feeling must be clarified by reason, reason must be guided by experiment'. Dr Gibbon's personal example was no less overwhelming because he had developed the heart-lung machine and performed the first successful open heart operation on heart-lung bypass after an experimental odyssey that spanned no less than two decades. When I chose cardiac surgery as my life-work after warming both hands in the fire of general surgery at the Postgraduate Medical Institute in Chandigarh, the imprint of experiment was still fresh on my mind. Appropriately enough, I learnt my first lessons in cardiac surgery in the Hunterian laboratory of the Johns Hopkins Hospital in Baltimore. Little did I realize then that my introduction to blood-compatible materials by Gott would bear upon my general approach to cardiac surgery and upon the course of my life.

2. Materials and blood compatibility

Prior to 1960, there was scarcely any progress in the development of materials with a blood-compatible surface. Not that efforts had not been made. Alexis Carrell had indeed noted in the early years of the century that paraffin coating would prolong the clotting time of blood in glass test tubes; later on, other observers had observed that silicone coating too would produce a similar effect. So long as the search for materials with a blood-compatible surface was confined to the physiological laboratory, it remained essentially a low-key affair. Once the experimental need was met by paraffin- or silicone-coated tubes, physiologists turned their attention to vascular homeostasis, which is another name for blood remaining fluid indefinitely within the cardiovascular system. Do the electronegative charge of the lining of blood vessels and the similar charge of the blood elements hold the key to vascular homeostasis? In that case, how does one explain the marked clot-inducing tendency of a glass surface, which carries a negative charge? If bioelectrical factors are not preeminent, do the naturally occurring anticoagulants, including heparan sulphate in the endothelium, ensure the fluidity of blood? Since clotting is more prone to occur in the sluggish veins than the pulsatile arteries, does stasis have a role in vascular homeostasis? So wondered the physiologists; whose studies remained a far cry from the development of new materials or surfaces. The picture changed dramatically in the 1950s when cardiovascular surgery made its triumphant advent. The need to replace damaged heart valves and diseased arteries became insistent and demanded materials with far greater, and more durable, blood compatibility than what siliconized materials could provide. In the heroic fifties, intrepid surgeons like Hufnagel, DeBakey and Vorhees pressed into use methyl methacrylate, polyester, nylon and other materials that had been newly developed for industrial applications. To everyone's surprise, these early cardiovascular implants functioned reasonably well. It did not take long for the pioneers to realize that the relative success of the first-generation implants had less to do with the blood compatibility of their surface than with their placement in the environment of high-velocity flow. A conduit made of polyester, for example, would remain patent indefinitely as a substitute in the aortic position, but would induce a clot within hours as a replacement of the inferior vena cava.

It was in this unpromising context that Gott made the serendipitous observation that heparin would bind to rigid materials and make their surface clot-repellent under given conditions (Gott *et al* 1961). His observation became a trail-blazer because no fewer than 20 surfaces with various degrees of antithrombogenicity were developed in the following two decades.

3. The GBH surface

In an attempt to reduce clot formation on artificial heart valves, Gott evaluated a number of materials and coatings by using an ingenious method. He placed small plastic rings constructed of many different polymers in the canine vena cava and found that most of the rings were fully or partly occluded by clots at the conclusion of the study. This was not surprising because the vena cava is a highly thrombogenic zone. What was surprising was the fact that methyl methacrylate rings coated with graphite stayed open for as long as 14 days. This was initially attributed to the known properties of graphite such as smoothness, inertness, conductivity and negative zeta potential. But subsequent studies revealed that the clot-repellent property of graphite was related to its ability to bind heparin when rinsed with a cationic surface-active agent (Gott *et al* 1965). The heparin bonding which took place in the laboratory was not the result of a planned exercise in surface engineering but the unintended outcome of a routine laboratory practice.

Every surgical laboratory has its rituals and protocols that are scrupulously followed in the performance of experiments. In Gott's laboratory where I worked, the graphite coating of plastic rings and other experimental components followed a strict protocol. Many colloidal graphite solutions are commercially available as industrial lubricants, and they consist of graphite particles of various sizes, a liquid plastic binder, and various hydrocarbon compounds that act as diluents and a vehicle for graphite (Gott *et al* 1968b). Colloidal graphite binds most satisfactorily to polymers that can be etched slightly by the solvent carrying the graphite particles. Our practice was to soak the rings, leaflets and other components in a colloidal graphite solution and dry them in a hot-air oven. This was followed by their immersion for several hours in a solution of benzalkonium chloride, a common hospital disinfectant that is also surface-active. Just before implantation in the animal, the devices were rinsed in heparin. The technique for applying the graphite coating on plastics and metals was simple except that it could be messy!

The new clot-repellent surface was given the self-explanatory term GBH (graphite-benzalkonium-heparin) surface. Figure 1 illustrates the proposed chemical arrangement of heparin and benzalkonium molecules on a graphite surface. Thanks to the adsorptive property of graphite, it firmly binds the cationic detergent benzalkonium chloride which has surface-active properties. In turn, the positively charged quaternary ammonium radical on the cationic detergent binds heparin, which is a polysaccharide containing three negatively charged sulphate groups per unit. The GBH surface is sufficiently stable to withstand the systemic challenge of protamine (Whiffen *et al* 1964) and retains 20% of the initial heparin activity even after 3 months in the venous circulation (Whiffen and Beckler 1966).

The clot-repellent effect of the GBH surface was further evaluated in a series of experiments where GBH-coated and uncoated leaflets of various plastic films were implanted in the canine right atrium (Valiathan *et al* 1966). The plastic films included

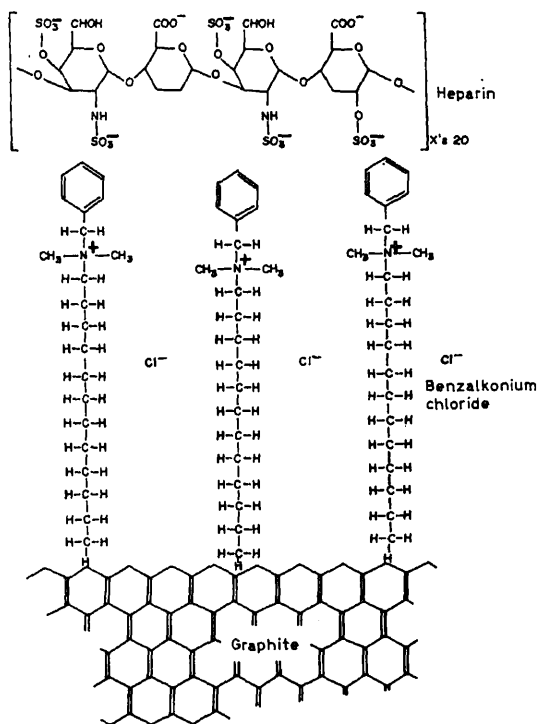


Figure 1. Scheme of GBH surface.

those of Teflon, Lexan, Tedlar, vinyl, Silastic and conductive vinyl. These studies showed that the plain plastic leaflets caused clotting in every instance (figure 2) whereas 17 out of 24 GBH-coated leaflets remained free from clot or thrombus (figure 3).

While the clot-repellent property of the GBH surface was no longer in doubt, we were aware of its drawbacks. In the first place, the heparin bonding was ionic and could not last indefinitely. Secondly, the graphite coating made blood conduits opaque and the visualization of air bubbles impossible. The surgeon could not therefore rule out the possibility of air embolism. Thirdly, the graphite blocked the diffusion of solutes if the GBH surface was to be used for dialysis. Lastly, the GBH coating could be applied only on metals or rigid plastics and could crack on the application of a lamp. Notwithstanding these defects, the GBH surface found applications in the Gott-Dagget valve, an experimental double-chambered artificial heart (Topaz *et al* 1967), and a technique for thoracic aortic bypass (Valiathan *et al* 1968). A brief description of this technique is not inappropriate because it continues to be in vogue.

Aneurysms are bulbous dilatations of arteries. When the arterial wall weakens owing to congenital defects, atherosclerosis or infection, the intraluminal pressure operates relentlessly according to the law of Laplace and produces a gradual, but progressive, increase in the diameter of the swelling and eventual rupture. If the lesion involves the aorta or the arteries of the brain the rupture is invariably fatal. Aneurysms of the aorta in the chest are not only vulnerable to fatal rupture; they also pose great difficulties in surgical resection. This is because the temporary interruption of blood



Figure 2. Uncoated plastic leaflet engulfed in thrombus.

flow, which is inevitable during surgery on the thoracic aorta, carries the extra danger of depriving the spinal cord of blood supply and causing paraplegia. To prevent this complication, the technique in the early sixties employed a temporary left heart bypass, complete with the arrest of coagulation in the patient with heparin, insertion of a temporary shunt between the left atrium of the heart and the femoral artery, and the use of an external pump (figure 4). Not only was this cumbersome, it also caused troublesome generalized bleeding due to circulating heparin. Obviously a temporary shunt from the aorta above the level of the aneurysm to a downstream location would have done the job just as well. If the need could be met locally without causing a major circulatory disturbance, so much better would the patient also be. To smoothen one's way, it is unnecessary to carpet a thorny path all the way; wearing shoes will do. But the localized approach had a catch: the temporary shunt should not clot during two or three hours when the aneurysm was being removed and the aorta reconstituted with a prosthetic graft. The GBH surface raised new hope, and we soon developed a GBH-coated shunt in the laboratory at the Hopkins for thoracic aortic bypass, which was subsequently used in patients with great success (Valiathan 1969) (figures 5, 6, 7).

Heparin bonding—after GBH

For all its drawbacks, the GBH surface excited much interest in heparin bonding. The structure of the heparin molecule made it an admirable plaything in the hands of chemists. Heparin is a polysaccharide, the bulk of the chain consisting of alternating units of uronic acid and glucosamine, bound in 1-4 linkages (figure 8). Most of the amino groups of the glucosamine residues are sulphated, only a minor proportion being acetylated. A variable fraction of the heparin chains are linked to serine or small peptides: in most tissues studied, it occurs primarily as single polysaccharide chains with molecular weight ranging from 5000 to 15,000. In addition to the single-chain type, a macromolecular form of heparin with much higher molecular weight also exists in tissues such as rat skin. Heparan sulphate, closely related to heparin, consists of a family of molecules in which deacetylation has occurred to a much less degree during biosynthesis. While heparin is stored in the granules of the mast cell, heparan sulphate is an ubiquitous component of the surface of many, if not all, cell types and is present in the form of a proteoglycan. Obviously this proteoglycan is different from heparin proteoglycan. Despite similarities in their polysaccharide components, they are distinct with respect to their core proteins. The presence of heparan sulphate on the endothelium perhaps contributes in no small measure to the fluidity of blood in the cardiovascular system. It is, so to say, a natural analogue of a heparinized surface.



Figure 3. GBH-coated plastic leaflet with no thrombus.

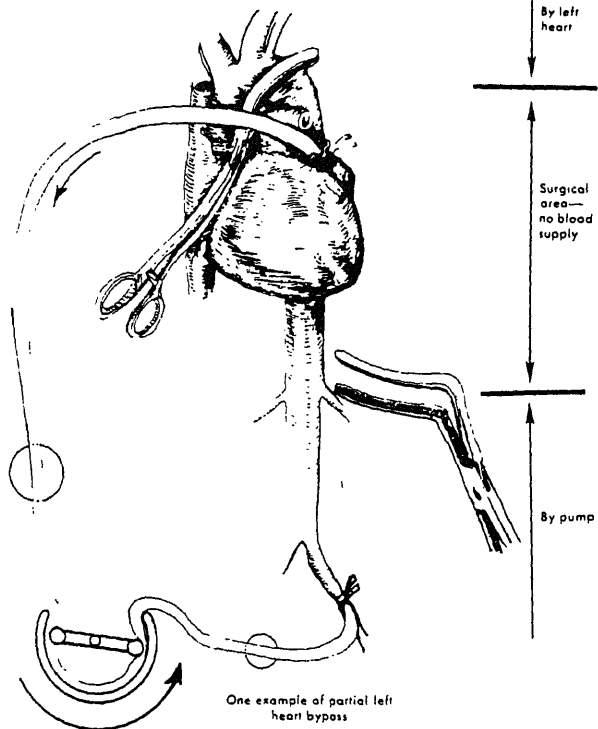


Figure 4. Conventional scheme for left atrium-femoral artery bypass.

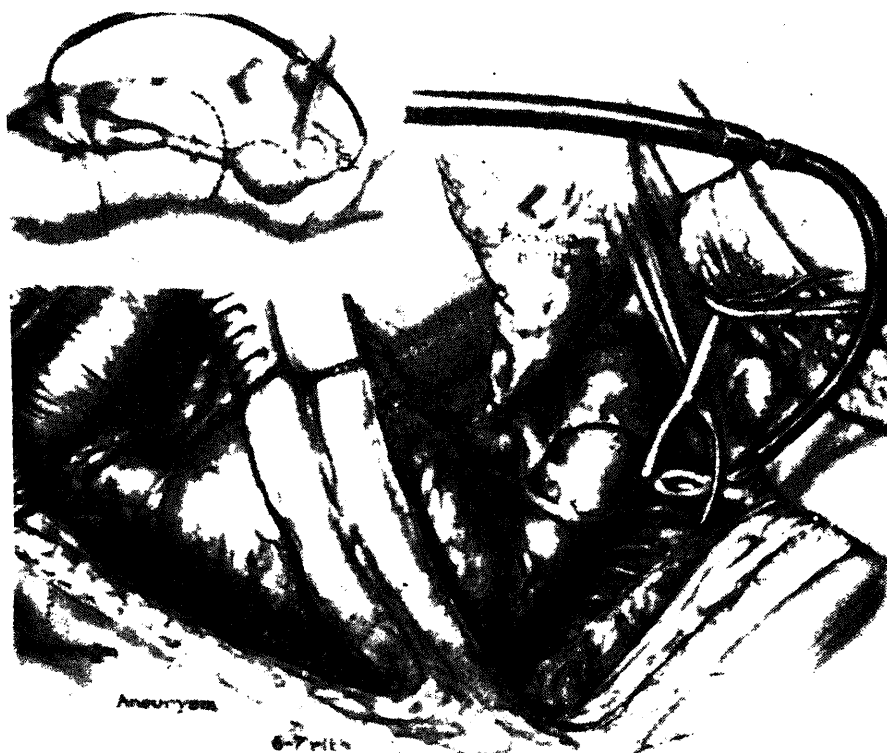




Figure 6. Shunt in position. Aneurysmal aorta being divided between clamps.

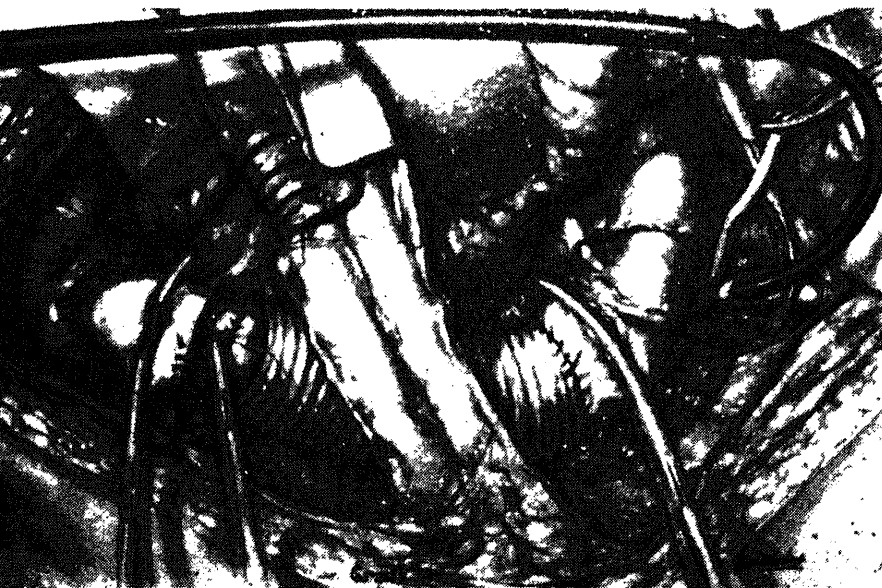


Figure 7. Aneurysm resection is over. Aorta being reconstituted by a polyester graft.

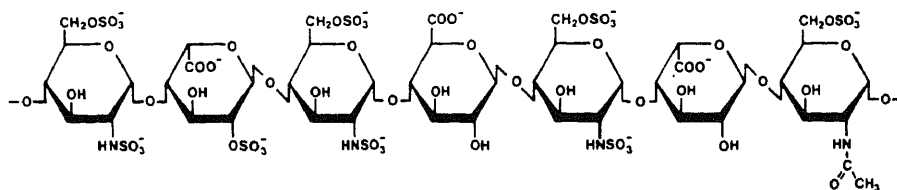


Figure 8. The repeating units in heparin.

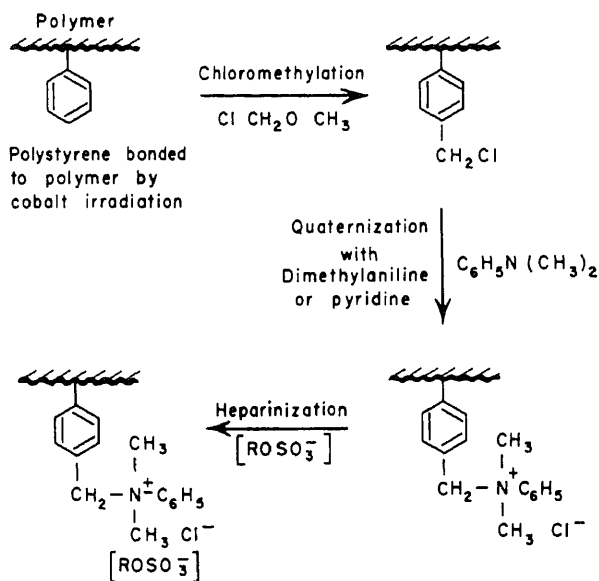


Figure 9. A scheme for heparinizing a nongraphited surface via chloromethylation and quaternization.

Since GBH demonstrated that negatively charged heparin reacts with positively charged quaternary ammonium salts, chemists devised methods to bond quaternary groups directly to a number of polymers prior to heparinization. Another method was to include a minor proportion of a quaternizable monomer such as vinyl pyridine in a polymer of interest and subsequently treat it for quaternization and heparinization (Leininger *et al* 1966). These and other techniques of surface modification yielded a large number of heparinized surfaces, which were studied for blood compatibility by placing the modified rings in the canine vena cava (Gott *et al* 1968a). Among the plethora of surfaces, investigators claimed to find antithrombogenicity in their respective creations, but lost all memory of it the next year! Perhaps the only surface to graduate from the experimental class was that developed by the Battelle Laboratories and applied subsequently in the celebrated Gott shunt (Gott *et al* 1966; Grode *et al* 1969). The Battelle surface utilized a cationic surfactant, tridodecylmethyl ammonium chloride (TDMAC), to bond heparin to the underlying polymer and eliminated the graphite layer (figure 9). This was the scenario a decade after GBH made its appearance.

Heparin bonding now

A decade, in my view, is too short a period for a biomedical idea to grow and fructify. This is because the ideas are far ahead of available technology, if not the understanding of contemporary scientists. Gibbon conceived heart-lung bypass, which had to wait for 20 years for realization. In 1955 Melrose introduced the concept of potassium cardioplegia, which was promptly discarded; it returned to change the face of cardiac surgery more than 20 years later. When one looks at Souttar's mitral valvotomy, Lillehei's technique for conserving the chordal mechanism during mitral-valve replacement, and many other examples, one is struck by the recurrence of the 20-year interval for the maturation of biomedical ideas. When I see the recent interest in transmyocardial puncture by Nd-YAG laser for myocardial revascularization, I tend to think that the time has come for the idea of the 'snake heart' operation which Prof. Sen advanced in the late sixties. Efforts in heparinizing polymer surfaces waxed in the late sixties and early seventies, but waned thereafter for 20 years, called the 'years of frustration' for work on blood-material interactions (Andrade *et al* 1981). Two decades later, heparin bonding has returned to occupy the centre stage of research in biomaterials.

The biological effect of heparin is primarily shown through its interaction with antithrombin. Thanks to the heavily sulphated residues, heparin binds to antithrombin with great affinity and accelerates the inactivation of coagulation factors, only a small fraction of the heparin molecule complexing with antithrombin. Since the earlier attempts to attach heparin by ionic bonding and surface grafting did not produce a stable linkage, efforts continued to couple heparin covalently through the carboxyl, hydroxyl and amino functions of the molecule. The resultant surfaces failed to show significant resistance to clotting, presumably due to the surface binding of the functional groups on heparin. However, Larm's description of what he called the 'end-point attachment of heparin' signalled a major departure in the method of heparin bonding (Larm *et al* 1983). Here, the chemical coupling took place at the terminal aldehyde group of reduced heparin without detriment to the anti-thrombin binding site of the heparin molecule. Reduced heparin is in the low-molecular-weight range of the heterogeneous family of heparins. Bound to prosthetic surfaces according to this method, heparin is stable and not leached on contact with blood or saline. Strongly anticoagulant, the orientation of the end-point-attached heparin on a surface resembles the distribution of heparan sulphate proteoglycan on cell surfaces (figures 10 and 11). The thromboresistant effect of end-point-attachment of heparin, which has the proprietary name 'Carmeda bioactive surface', is far higher than the thrombin-inhibiting capacity of ionically bound heparin. The Carmeda surface is claimed to have a shelf life of 2 years.

The impact of the new bioactive surface of heparin on surgical practice has been considerable. In the first place, it has reduced the requirement for heparin and its neutralization by protamine during prolonged heart-lung bypass. Secondly, it has proved to be far gentler to blood than untreated surfaces in so far as it activates neutrophils and C3 complement to a much less degree (Nilsson *et al* 1990) and reduces platelet count even less (Segesser *et al* 1990). The promise of biocompatibility of the Carmeda surface has been such that it has even been applied on implantable lenses to reduce the adherence and growth of cells.

The heart-lung bypass systems, including centrifugal pumps, which feature the

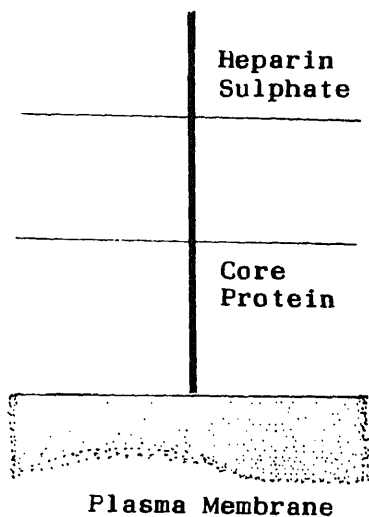


Figure 10. A diagram to show the distribution of heparin and heparinoid molecules on cell surface.

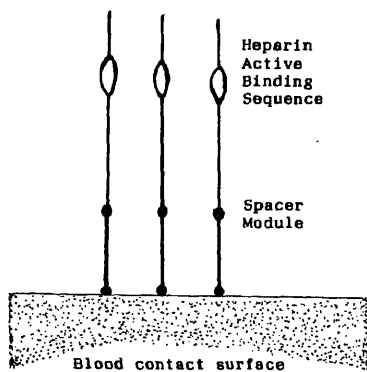


Figure 11. The new technique for creating heparin-active binding sequence. Note the similarity to figure 10.

new bioactive surface of heparin are costly, as new medical devices always are. Their cost-benefit analysis is a subject of ongoing debate in Western countries. But, to paraphrase Fermi, where do we, in India, come in? Over the past decade our group in Trivandrum developed and transferred for production a series of blood-contacting devices including the blood bag, oxygenator, cardiectomy reservoir and the heart valve. Soon a vascular graft will join the list. Two things common to them are the need for blood contact in clinical use and the need for import at high cost. Without exception, they are based on materials that have stood the test of time in surgical use. As such their biocompatibility and degree of medical safety are perfectly acceptable by contemporary standards. But in medical technology, as indeed in other branches of technology, a given product or process is no more than a stage in a never-ending process of evolution. Endowed with a heparinized surface, each of our devices will improve in function and pave the way for a new generation of advanced

devices. The blood bag (Pal *et al* 1988), for example, is made of sheets extruded from PVC compound that differs little from the material used in other commercially available blood bags. If the blood-contacting surface of the bag is heparinized covalently, the preservation of blood elements, including platelets and serum proteins, could substantially improve and this would lengthen the safe storage period of blood. This is no small thing because the cellular components are literally thrown away at present after three weeks of storage, not to speak of the need to check the level of potassium before administering the plasma.

The oxygenator is the central unit of the heart-lung bypass system, which includes lengthy conduits of PVC tubes, a cardiectomy reservoir to receive blood from the heart chambers, and a pump (Venkatesan *et al* 1981, 1983; Valiathan 1985; Nazer *et al* 1991). The oxygenator is basically a disposable device which removes carbon dioxide from the venous blood and adds oxygen to it. It is perfectly efficient in terms of gas exchange during heart-lung bypass even though it can hardly compare with the lungs in surface area or blood compatibility. Since our oxygenator employs the bubble principle, which involves the bubbling of oxygen through a column of venous blood and the subsequent removal of excess bubbles by cascading the oxygenated blood over a defoaming substrate, its blood-contacting surface is quite large. Added to this are the surfaces of the cardiectomy reservoir and the lengthy conduits, which together must permit five litres of blood to pass through the system every minute. It is a tribute to the toughness and self-regenerative capacity of our tissues that the damage suffered by the cellular elements and serum proteins of blood after 3–4 hours of heart-lung bypass remains modest and reversible. One might say that the heart-lung bypass succeeds more by nature's healing processes than by our success in surface engineering! But even the modest damage to blood can cause morbidity, complications and prolongation of recovery. If the surface of the extracorporeal system had a stable, heparinized surface, heart-lung bypass for several hours could be far less traumatic to blood. This has been demonstrated by the Carmeda experience.

The artificial heart valve poses a different problem (Valiathan *et al* 1978; Valiathan and Bhuvaneshwar 1982; Bhuvaneshwar *et al* 1983a, 1991; Lal *et al* 1984; Valiathan 1993). Here is a device which consists of a housing made of Haynes 25 alloy, a tilting disc of ultra-high-molecular-weight polyethylene, and a sewing ring of polyester cloth. Unlike the blood bag and oxygenator, it is a permanent cardiac implant which must open and close 100,000 times a day for many years without mechanical failure. A problem that continues to bedevil the mechanical valves is the formation of clots on the non-moving components of the valve and the obligation for the patients to take anticoagulant medications. The ring of plastic fabric which is sewn to fix the valve to the margins of the excised valve provides the most vulnerable site for the formation of clots. It is entirely possible that a heparinized surface on the sewing ring may further reduce the already low rate of thromboembolism and make mechanical valves safer.

Vascular grafts are seamless, crimped tubes woven or knitted from polyester yarn (Bhuvaneshwar *et al* 1981, 1983b). They function very well as replacement for arteries larger than 10 mm in diameter and save the lives and limbs of thousands of patients all over the world every year. Unfortunately their long-term patency rate drops sharply as the diameter of the artery becomes smaller and they are poor substitutes indeed for vessels as small as the carotid or the coronary arteries. Vascular surgery has failed to breach the 10 mm barrier despite much effort. The effect of heparin

bonding of the graft on the long-term patency of small-diameter grafts is therefore of great interest.

These are by no means the only examples of the clinical promise of heparinized surfaces. As we learn more of the biological role of heparins and the technology for heparin bonding improves, heparin-bonded surfaces will cast their mantle on not only cardiovascular but other devices as well. After all the distribution of heparan sulphate is not confined to the cardiovascular system.

6. Conclusion

The story of heparin bonding is typical of what is happening in biomaterials science. The long search for inert materials is giving way to the development of bioactive surfaces thanks to the realization that no surface in the body is inert. The change in direction from inertness to bioactivity is unmistakable.

The early hunters for a blood-compatible surface were exact men who wished to copy nature. But wherever they went, vibrant vessels vanished, filmy leaflets of heart valves died, the shining intima ceased to exist, and the grace and splendour of nature's handiwork were transformed into painted pipes, one-way check valves and plastic fabrics, which were studied and described in the greatest detail. The varied designs and the magic of self-renewal disappeared during their experiments, which turned the living celebration of nature into a mixture of chemical processes and cunning devices. When the point of disenchantment was close, the call has come for a return to nature. For none can deny that the attachment of heparin or albumin or cells to surfaces is no more than a humble attempt to clothe non-living materials in natural garments. To the extent the effort succeeds, we shall have triumphed in making materials biocompatible and medical devices safe.

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Positron annihilation spectroscopy in materials science

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Abstract. The application of positron annihilation spectroscopy to the study of defects in materials is illustrated through several examples drawn from our work. These include the study of vacancy clustering in metals, clustering of He atoms to form bubbles, and solute clustering in alloys. Results of studies on novel materials such as quasicrystals, cuprate superconductors and fullerenes are also presented.

Keywords. Positron annihilation spectroscopy; clustering; helium bubbles; quasicrystals; cuprate superconductors; fullerenes.

Introduction

When energetic positrons from a radioactive source enter condensed medium, they rapidly lose their energy by collisions with electrons and ions. After a somewhat longer period, characteristic of the medium, their annihilation is announced by the emergence of energetic photons, whose energy, momenta and time of emission can be measured with great precision with modern detector systems. The utility of positron annihilation studies of condensed matter (for reviews see: West 1973; Brandt and Rupasquier 1983) relies on the fact that, while in principle the characteristics of the annihilation process involve sophisticated considerations of quantum electrodynamics, nevertheless depend almost entirely on the initial state of the positron-electron system. In perfect crystalline materials, the positron exists in a periodic Bloch state, and from a measurement of the momentum of the annihilation photons, information on the electron momentum distribution can be obtained. This forms the basis of an important area of application of positron annihilation to the investigation of electronic structure (Berko 1983) of materials. In the presence of defects, in particular vacancy-type defects, positrons are trapped at these sites and the resultant annihilation characteristics can be used to characterize the defect (Nieminen 1983). In the last two decades, these two streams of applications have been refined and several detailed and interesting studies pertaining to electronic structure and defect properties of materials have been carried out. In this article, the application of positron annihilation spectroscopy (PAS) to defects is emphasized with example drawn from our own work.

The format of this paper is as follows: In §2 a brief introduction to the positron annihilation technique is provided, following which the physical basis for the investigation of a variety of defect-related phenomena are presented in §3. The application of PAS to the study of clustering of vacancies, helium in metals, and solute clusters is discussed in the subsequent sections. The last decade has seen the discovery of several new classes of materials such as quasicrystals, high-temperature superconductors, fullerenes, etc. In all these materials, PAS has been used with a view to obtain information on structure and electronic properties. Our own efforts in this direction are contained in §4. Finally a summary and future outlook are presented.

2. Positron annihilation spectroscopy

The basic aspects of PAS (West 1973) can be best explained with the help of the schematic shown in figure 1. Positrons emitted from a radioactive source such as $^{22}\text{NaCl}$ are injected into the solid, wherein they thermalize and annihilate with one of the electrons in the medium resulting in the emission of two annihilation photons of 0.511 MeV ($=m_0c^2$). The annihilation rate (inverse of lifetime) is determined by the electron density at the site of the positron; in metallic systems the lifetime is $\sim 150\text{ ps}$. Positron lifetime measurements are carried out by measuring the time delay between the 1.28 MeV gamma ray which signals the birth of the positron and the 0.511 MeV annihilation photons using ultrafast timing methods derived from nuclear spectroscopy. The annihilation radiation also carries information concerning the momentum of the electron-positron pair. Due to the momentum of the electron-positron pair, which is mainly due to the motion of electrons in the material, there is a slight departure of a few milliradians from collinearity. Thus, from a measurement of the angular correlation of the annihilation radiation, information concerning the electron momentum distribution and Fermi surface can be obtained. Another consequence of the momentum of the annihilating electron-positron pair is the Doppler broadening of the annihilation radiation lineshape which can be measured using a high-energy resolution germanium detector.

3. Defect spectroscopy with positrons

In a perfect crystal, the positron moving in the periodic potential of ions and electrons exists in a periodic Bloch state. Due to strong Coulomb repulsion from the positive-ion cores, the positron density distribution has a maximum in the interstitial regions

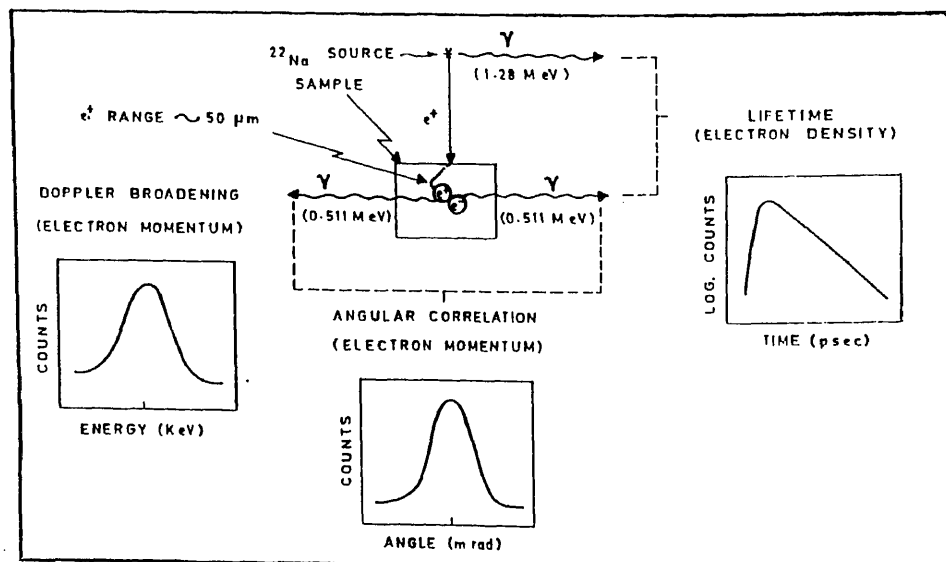


Figure 1. Schematic of positron annihilation spectroscopy.

and the positron mainly annihilates with the valence electrons with a small contribution from the core electrons. Positron behaviour in crystalline materials is drastically affected in the presence of vacancy-type defects. The absence of ion core results in a strong attractive potential for the positron at which it is trapped (Nieminen 1983). At vacancy-type defects, the total electron density is smaller than in the bulk crystal, which leads to an increase in lifetime. With increase in the concentration of defects (beyond 10^{-7}) an increasing fraction of positrons are trapped at defects, and finally at concentrations greater than 10^{-4} all the positrons annihilate from the trapped state. The changes in the annihilation characteristics with defect concentration are described quantitatively in terms of the trapping model (West 1973; Brandt and Dupasquier 1983). From a study of the variation of annihilation characteristics with temperature, the evolution of equilibrium vacancy concentration with temperature can be followed and this forms the basis of one of the most precise methods for the determination of vacancy formation energy.

The annihilation characteristics of the positron trapped at defects is sensitively dependent on the size and even geometry of defect clusters (Nieminen 1983). For example, with increase in the size of the vacancy cluster, the positron gets more localized at the defect and consequently overlaps less with the electron distribution around the defect. This results in an increase in the lifetime with the size of the defect cluster. The association of the experimentally measured lifetime with a specific defect is made possible by developments in the theoretical calculations of positron density distribution and annihilation characteristics at defects (Puska and Nieminen 1983; Bharathi 1988). Briefly, these calculations proceed by numerically solving the Schrödinger equation for the positron with the positron potential given as a superposition of the Hartree electrostatic potential and the electron-positron correlation energy. The annihilation rate is then evaluated from the overlap of the positron density with the enhanced electron density at the site of the positron. Such calculations have now been carried out for a variety of defects such as monovacancies, vacancy clusters, decorated vacancy clusters, solute clusters, etc. Figure 2 shows the calculated values (Amarendra *et al* 1992) of positron lifetimes as a function of the size of vacancy cluster in Ni. Also shown in the figure is the reduction lifetime with He decoration

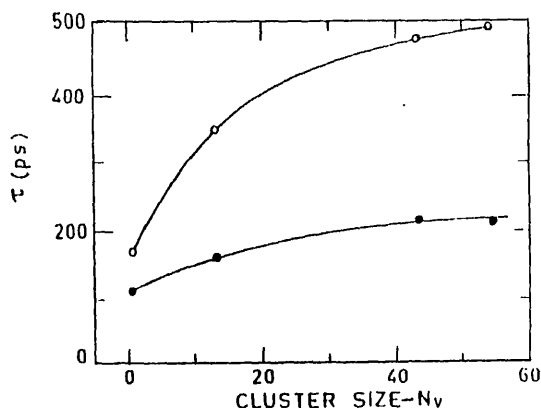


Figure 2. Variation of positron lifetime as a function of cluster size in a pure vacancy cluster (○) and at a He-decorated vacancy cluster (●) (From Amarendra *et al* 1992).

of the vacancy cluster. The extreme sensitivity of the positron lifetime to the size of small vacancy clusters and the influence of decoration with gas atoms has been exploited in the study of vacancy clustering in metals (Sundar *et al* 1986) and in the investigation of nucleation and growth of helium bubbles in alpha-irradiated metals (Viswanathan and Amarendra 1990; Gopinathan and Rajaraman 1994). The annihilation characteristics are also seen (see §3.3) to be sensitive to the presence of small solute clusters in quenched alloys, and this has been used (Bharathi 1988) in the study of early stages of phase separation in quenched alloys. An illustrative example of each of these studies is presented in the following.

3.1 Vacancy clustering in metals

The evolution of defect structure in cold-worked Ni with temperature has been monitored (Sundar *et al* 1986) by positron lifetime measurements as a function of isochronal annealing temperature. The measured lifetime spectra have been analysed in terms of two lifetime components τ_1 and τ_2 , and the intensity of the second component I_2 , and the results are shown in figure 3. In the temperature range up to 160°C, the lifetime spectrum has a single component of 170 ps, which can be associated (c.f. figure 2) with the annihilation at monovacancies and dislocations. In the temperature range 160–400°C, the lifetime and intensity of the second component increases. The increase in τ_2 signals the agglomeration of mobile vacancies resulting in the formation of vacancy clusters (c.f. figure 2). In addition to the above mentioned

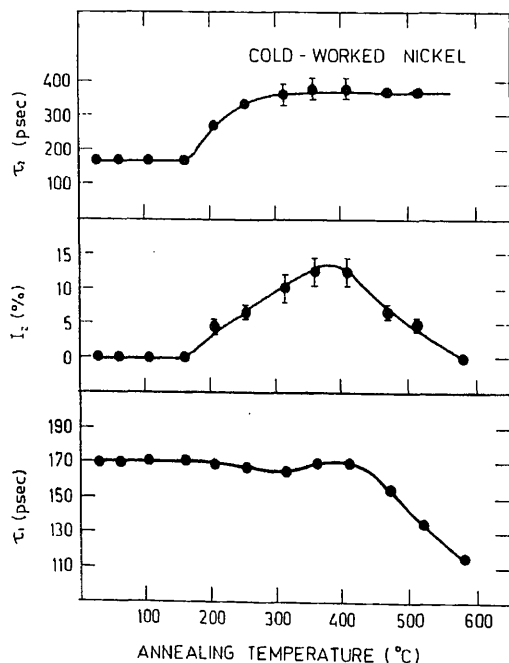


Figure 3. Variation of lifetime parameters as a function of isochronal annealing temperature in cold-worked Ni (From Sundar *et al* 1986).

isochronal annealing experiments, through isothermal annealing experiments, the kinetics of clustering of vacancies has been studied. Further, the observed variation of positron lifetime with annealing temperature and time has been quantitatively understood (Sundar *et al* 1986) by modelling the evolution of vacancy clusters using chemical-kinetic rate equations coupled with the theoretically calculated values of positron lifetime vs cluster size as shown in figure 2.

The above example illustrates how the results from positron lifetime experiments can be used to derive information about the evolution of small vacancy clusters with annealing temperature and time. Extensive studies on the clustering of vacancies during isochronal annealing have been carried out in pure metals and to study the influence of substitutional and interstitial impurities (Kajcsos and Szeles 1992). Several experiments have also been carried out on technologically important materials such as stainless steels (Viswanathan 1989). A recent example of such a study is the investigation of the formation of TiC precipitates, which play an important role in improving the radiation resistance of stainless steel (Rajaraman *et al* 1994a).

3. Helium clustering in metals

The introduction of helium into metals by direct injection or by (n, α) reactions, occurring during neutron irradiation in a reactor, leads to several deleterious effects such as the nucleation and growth of voids, embrittlement, and blistering of metal surfaces (Donnelly and Evans 1991). The clustering of helium atoms to bubbles proceeds through the formation of $\text{He}_m\text{-V}_n$ complexes, which act as bubble nuclei, and these grow by the migration and coalescence or Ostwald ripening process. PAS with its sensitivity to small helium-decorated vacancy clusters can be used to follow the evolution of He clusters (Viswanathan and Amarendra 1991; Gopinathan and Rajaraman 1994). This is illustrated by the results of isochronal annealing studies (Amarendra *et al* 1992) in alpha-irradiated Ni shown in figure 4. In the as-irradiated state, a shorter lifetime of 140 ps with 70% intensity and a longer lifetime of 240 ps with 30% intensity are seen. On the basis of theoretical calculations of positron lifetime, the shorter lifetime can be associated with He_4V complexes whereas the longer-lifetime component to small vacancy clusters containing about five vacancies. An important feature of the annealing curve shown in figure 4 is that between 500 and 750 K τ_1 decreases sharply towards the bulk value. τ_2 decreases exhibiting a minimum, and I_2 increases to a maximum. These trends in lifetime parameters can be understood (Amarendra *et al* 1992) as due to helium decoration of vacancy clusters leading to the formation of stable bubble nuclei. The increase in τ_2 and the corresponding decrease in I_2 beyond 750 K correspond to the growth in size of bubbles with a decreasing concentration. Thus from isochronal annealing experiments, the stages corresponding to the nucleation and growth of helium bubbles can be identified.

The measured positron parameters can be used to obtain the bubble parameters, viz. the concentration (C_B), radius (r_B) and helium atom density (n_{He}), on the basis of the positron surface state model (Jensen and Nieminen 1987). According to this model, the annihilation rate of the positron trapped within the helium bubble is determined both by its overlap with the bubble surface and the helium atom density within the bubble. Further, the fraction of positrons trapped inside the bubbles is dependent

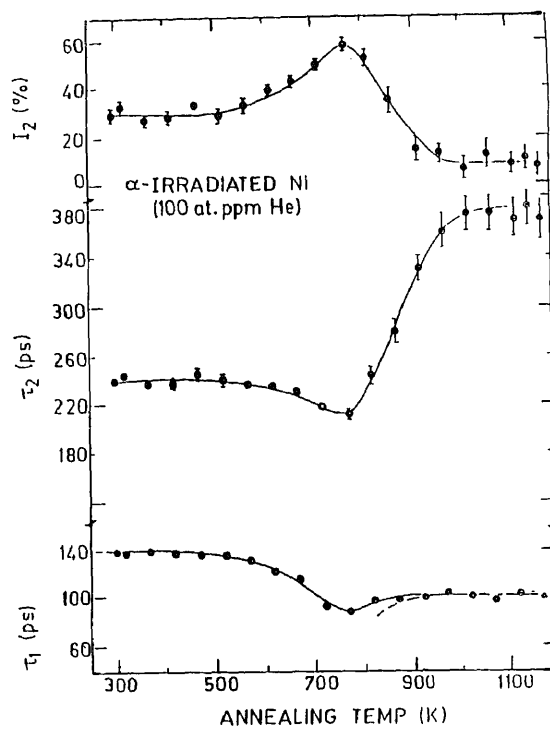


Figure 4. Variation of lifetime parameters as a function of isochronal annealing temperature for α -irradiated Ni (100 at. ppm He). The dashed line indicates τ_1 value evaluated using the two-state trapping model (From Amarendra *et al* 1992).

on both the bubble concentration and radius. This, together with the helium inventory equation, can be used to obtain (Viswanathan and Amarendra 1991) both C_B and r_B . The results of such an analysis carried out in the case of Ni are shown in figure 5. Studies on helium bubble growth have been carried out to investigate the effect of irradiation temperature, dose, the influence of impurities, etc and studies on the kinetics of bubble growth have also been carried out (Amarendra 1990; Amarendra *et al* 1992; Rajaraman 1993; Rajaraman *et al* 1994b). In recent experiments on α -irradiated Pd (Rajaraman *et al* 1994b) coupled with theoretical modelling, the influence of helium density on bubble growth kinetics has been established. The detailed studies on the evolution of He clusters has been one of the fruitful applications of PAS.

3.3 Solute clustering in quenched alloys

The study of early stages of clustering of solute atoms in alloys resulting in the formation of precipitates has been a topic of considerable interest in physical metallurgy (de Fontaine 1975) and has been extensively investigated by diffraction methods and microscopy. As a result of experimental and theoretical studies carried out in our laboratory (Bharathi 1988; Bharathi and Chakraborty 1988), it has been

shown that PAS can be profitably used to investigate this phenomenon. The sensitivity of positrons to the formation of solute clusters accrues from the preferential affinity of the positron to one of the constituents of the binary alloy, such as Ag in Al–Ag alloy. Thus, if the Ag atoms cluster together, then the attractive potential for the positron may become large enough to completely localize the positron at the Ag cluster. The annihilation characteristics are seen to be sensitive to the size, geometry and composition of the solute cluster in alloys (Bharathi 1988; Bharathi and Sundar 1988, 1992). Figure 6 shows the sensitive dependence of the lifetime as a function of the size of Ag cluster in Al matrix. The lifetime starting from a value characteristic of pure Al decreases towards bulk Ag value as the cluster size increases.

The results of *in situ* Doppler broadening lineshape measurements in quenched Al–1% Ag alloy are shown in figure 7. In the as-quenched alloy the lineshape parameter is close to that in Ag. This can be understood in terms of positron trapping and annihilation from Ag-rich Guinier–Preston (GP) zones. In the temperature range 100–200°C the lineshape parameter sharply increases and subsequently merges with

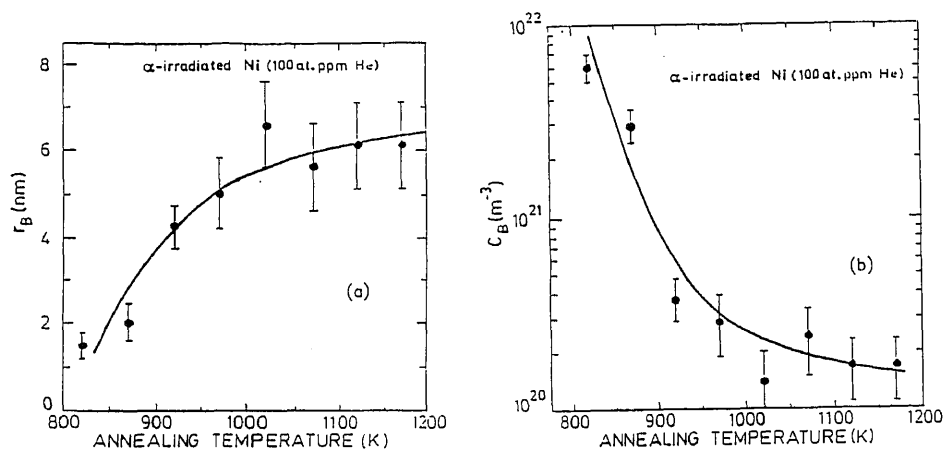


Figure 5. Variation of (a) the He bubble radius r_B and (b) bubble concentration C_B as a function of annealing temperature as obtained from the analysis of data shown in figure 4.

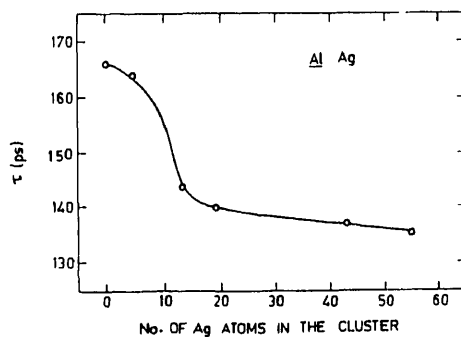


Figure 6. Theoretically calculated variation of positron lifetime as a function of the size of Ag cluster in Al matrix (From Bharathi and Sundar 1988).

results for pure Al. This sharp increase in the I parameter is associated with decrease in Ag content of GP zones rather than coarsening, leading to reduction in the number density of GP zones. From the measured value of the I parameter, the composition of GP zones at various temperatures can be obtained, and this provides a novel method for determining the GP zone solvus (Bharathi and Sundar 1988). The results obtained from positron experiments are shown in figure 8. In view of the inherent sensitivity of positrons to vacancies, the role of quenched-in vacancies in the formation

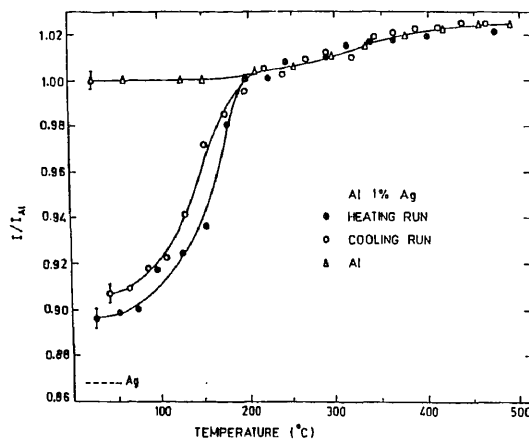


Figure 7. Temperature dependence of Doppler lineshape parameter, with reference to Al, in Al-1% Ag alloy (From Bharathi and Sundar 1988).

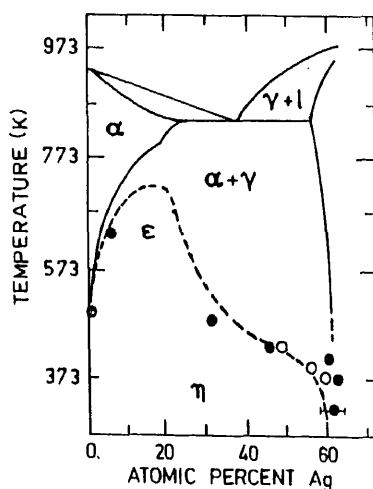


Figure 8. Phase diagram of Al-Ag alloy, in which the data obtained from Doppler measurements in Al-1%Ag (closed circles) and Al-6%Ag (open circles) alloy are plotted. These data points are obtained by analysis of the lineshape parameter in the alloy in terms of the weighted average of the lineshape parameter in Al and Ag (From Bharathi and Sundar 1988).

of GP zones can be investigated. In addition to the study of the early stages of the clustering process, PAS can also be used to investigate the later stages of precipitation process by probing the defects generated at the interfaces of the precipitate/matrix interface, as has been carried out in Al–22% Zn alloy (Bharathi *et al* 1988a).

4. Studies on novel materials

Apart from the above examples of using PAS as a tool for detailed studies of defects in crystalline metals, in our laboratory accent has also been on the application of PAS to the investigation of defects and electronic properties of novel materials. Following this approach, several studies have been carried out on metallic glasses (Gopinathan and Sundar 1984), quasicrystals, cuprate superconductors, and, recently, fullerenes. An account of some of the salient results is presented in the following after a brief background of the interest in the particular system.

4.1 Quasicrystals

Quasicrystals represent a new class of ordered structures wherein there is long-range translational order and crystallographically forbidden rotational symmetry and there has been a tremendous interest in trying to understand the atomic structure and stability of quasicrystals (DiVincenzo and Steinhardt 1991). In addition to diffraction methods, several experimental techniques which are sensitive to the local structure have been employed and these have played a valuable role in establishing the existence of similar icosahedral clusters, such as the MacKay icosahedron, in both the quasicrystalline phase and crystalline approximants (Goldman and Kelton 1993). It is of interest to know if positrons are trapped at the central vacant site of this cluster and thus provide information about the local structure. A priori, this has been the motivation for positron studies in several quasicrystalline systems, such as Al–Mn, Al–Mn–Si, Al–Li–Cu and Al–Cu–Fe. Chidambaram *et al* (1993) observed the presence of a second lifetime component corresponding to small vacancy clusters, of a few ppm concentration, and this has been used to argue in support of the icosahedral glass model rather than models based on Penrose tiling.

In our experiments (Sundar *et al* 1991a), *in situ* measurements of positron lifetime as a function of temperature have been carried out in Al–Cu–Fe and the results are shown in figure 9. The lifetime is seen to show a reversible increase in two steps with a plateau in the range 250–400°C. From studies on several Al–Cu–Fe systems of different compositions, coupled with X-ray diffraction measurements, it has been shown that this reversible behaviour is due to positron trapping at thermally generated phason disorder. As is well known, the presence of phason disorder (Goldman and Kelton 1993) corresponds to flipping of long and short sequence of the ideal Fibonacci sequence and such a flipping can lead to a clustering of long segments. In the context of positron experiments, a clustering of long segments will lead to a local increase in the open volume regions and can account for the increase in lifetime with temperature. It would be interesting to carry out high-resolution positron-lifetime experiments, coupled with theoretical modelling, that could discriminate between thermal vacancies and phason disorder. This will be of great value in separating the

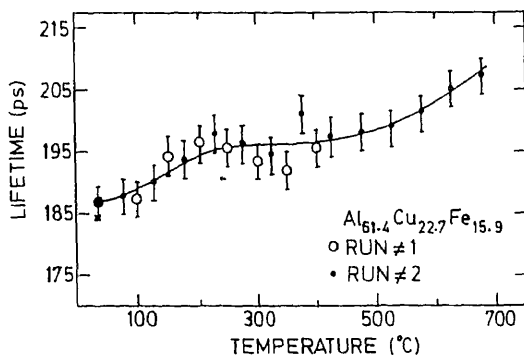


Figure 9. Variation of positron lifetime as a function of sample temperature in quasicrystalline $\text{Al}_{61.4}\text{Cu}_{22.7}\text{Fe}_{15.9}$ (From Sundar *et al* 1991a).

entropic contributions from vacancies and phason disorder to the stability of quasicrystals (DiVincenzo and Steinhardt 1991).

4.2 High-temperature superconductors

The discovery of high-temperature superconductors (HTSC) has initiated enormous activity (Muller and Olsen 1988), both theoretical and experimental, to understand the normal and superconducting states in these systems. PAS has been extensively applied to the study of these materials (for earlier reviews see: Sundar *et al* 1990a; Sundar and Bharathi 1991) and these studies can be broadly classified into (i) studies on the temperature dependence of annihilation characteristics across T_c , (ii) studies on structure and defect properties, and (iii) investigation of Fermi surface in these materials.

4.3 Temperature dependence of positron annihilation characteristics across T_c

The motivation for the studies on the temperature dependence of positron annihilation characteristics has been to see if the annihilation characteristics show any changes across T_c and can provide a clue to the mechanism of superconductivity. The first measurement of the temperature dependence of annihilation characteristics across T_c in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Y 1:2:3) was carried out by Jean *et al* (1987). In the ceramic superconductor, the positron lifetime and the Doppler lineshape parameter I were observed to decrease below T_c , whereas no such change was seen in the oxygen-deficient nonsuperconducting compound. Since these early measurements, there have been several studies on the Y 1:2:3 system and other cuprate superconductors (for reviews see Sundar *et al* 1990a). While most of the measurements in Y 1:2:3 indicated a decrease in positron annihilation parameters below T_c , in some experiments different kinds of temperature dependences were observed. This has caused considerable confusion in identifying the intrinsic temperature dependence associated with the superconducting transition in HTSC materials. It is plausible that these different temperature dependences arise due to the difference in the disposition of positron

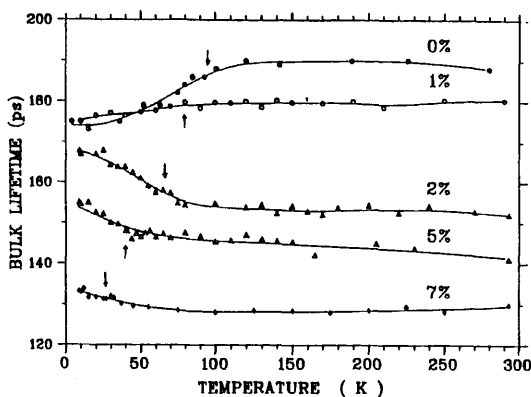


Figure 10. Variation of positron lifetime as a function of temperature in undoped and Zn-doped Y 1:2:3. The arrows are marked at T_c (From Jean *et al* 1990).

density distribution (PDD) with respect to the superconducting Cu–O planes and chains which are the dominant structural features of the Y 1:2:3 structure. In order to check this hypothesis, controlled experiments (Jean *et al* 1990) on undoped and Zn- and Ga-doped Y 1:2:3, coupled with theoretical calculations (Bharathi *et al* 1990) of the PDD, were carried out. Figure 10 shows the results of the experiments on Y 1:2:3 doped with various levels of Zn. It is seen that the decrease in bulk lifetime seen in undoped Y 1:2:3 reverses to an increase in lifetime in Zn-doped Y 1:2:3. Thus, in the same set of controlled measurement, different temperature dependences were observed, and the variation of lifetime in all cases is seen to be correlated with T_c , which decreases with increase in Zn content.

PDD in Y 1:2:3 has been obtained (Bharathi *et al* 1990) by solving the Schrödinger equation with the positron potential obtained using the potentials and electron densities from the orthogonalized linear combination of atomic orbitals (OLCAO) band structure calculations. In addition to the calculations of PDD, the electron–positron overlap function, which provides information on the contribution to annihilation from the various atoms in the unit cell, has also been calculated and these results are shown in figure 11. From these, it is seen that in undoped Y 1:2:3, wherein a decrease in lifetime is observed, the PDD is mainly in the region of Cu–O chains and the annihilation is dominated by the apical oxygen atom. In the Zn-doped Y 1:2:3, wherein an increase in lifetime is observed, there is a significant positron density in the Cu–O planes and the annihilation has large contribution from the planar oxygen atom. With this information, the different temperature dependences, i.e. both a decrease in lifetime as in undoped Y 1:2:3 and an increase in lifetime as in Zn-doped Y 1:2:3, can be consistently explained (Bharathi *et al* 1990; Jean *et al* 1990) in terms of an electron transfer from the planar O atom to the apical O atom. This is schematically shown in figure 12. An electron transfer from the planar to apical O atom will lead to a decrease in lifetime in undoped Y 1:2:3 since the annihilation is dominated by the apical O atom. A similar transfer of electrons will in the case of Zn-doped Y 1:2:3 contribute to an increase in lifetime since there is significant annihilation from the O atoms of the Cu–O layer.

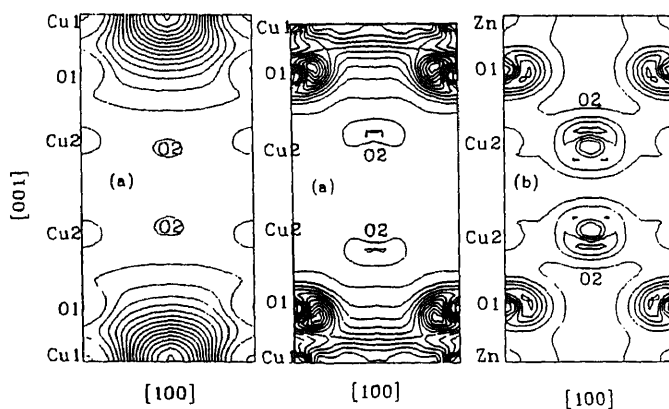


Figure 11. (a) Contour plot of the positron density distribution in the (010) plane of undoped Y 1:2:3. The maximum in the density is between the Cu(1) atoms and the contour spacing is $0.005 e^+/\text{a.u.}^3$. (b) Contour plot of the electron-positron overlap in the (010) plane of undoped Y 1:2:3, showing the maximum at the apical oxygen atom, O(1). (c) Overlap function in the (010) plane of Zn-doped Y 1:2:3, indicating contributions from both the apical and planar oxygen atom O(2). The contour spacing is $0.05 \text{ ns}^{-1}/\text{a.u.}^3$ (From Bharathi *et al* 1990).

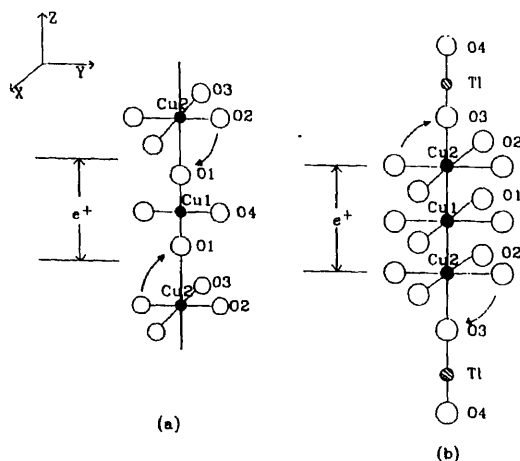


Figure 12. Schematic diagram of the local electron transfer from the planar to apical oxygen atom in (a) Y 1:2:3 and (b) Tl 2:2:2:3. The band shows the range of PDD (From Bharathi *et al* 1990).

Experiments on the temperature dependence of lifetime across T_c have also been carried out in other cuprate superconductors: $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Sundar *et al* 1990b), La-Sr-Cu-O (Jean *et al* 1988), Tl-Ba-Ca-Cu-O (Sundar *et al* 1990c) and Bi-Sr-Ca-Cu-O (Sundar *et al* 1991c). The variety of temperature dependences of lifetime seen in the various cuprates can be rationalized when the results are analysed in terms of PDD and the electron-positron overlap function. These calculations show

that the positron's sensitivity to superconductivity arises primarily from the ability to probe the Cu-O network in the Cu-O layer. The different temperature dependences of lifetime, i.e. both the increase and decrease, can be understood in terms of a model of local electron transfer from the planar oxygen atom to the apical oxygen atom, after taking into account the correct PDD within the unit cell of the cuprate superconductor. It may be remarked that the notion of charge transfer, as used to interpret the positron annihilation data, has also been used to explain several other experimental results in HTSC and also forms the basis of several theoretical models of superconductivity (Bishop *et al* 1989).

4.4 Defects and structural studies

It is well known that in HTSC materials, the defects and in particular the oxygen vacancies play an important role in controlling the structure and superconducting properties (Jorgensen 1991). On quenching the superconducting orthorhombic Y 1:2:3 from elevated temperatures, the oxygen atoms are known to be depleted from the basal plane, containing the Cu-O chains, resulting in the formation of non-superconducting tetragonal phase. In the Y 1:2:3 system, the positron density is in the region of the Cu-O chains (c.f. figure 11a) and the annihilation characteristics are sensitive to the oxygen stoichiometry and the ordering of O atoms in the basal plane (Bharathi *et al* 1988c). This has been used in the study of the orthorhombic-to-tetragonal structural transition occurring with increase of quench temperature (Bharathi *et al* 1988b; Sundar and Bharathi 1991), and the results are shown in figure 13. Also shown in this figure are the results for $\text{NdBa}_2\text{Cu}_3\text{O}_{7-x}$ (Sundar *et al* 1991b). The lower orthorhombic-to-tetragonal structural transition temperature in this system can be understood in terms of weakening of the O-O interaction in the basal plane arising due to the larger lattice parameters of the Nd-Ba-Cu-O system compared to Y 1:2:3.

The sensitivity of positron annihilation characteristics to the various ordered phases of Y 1:2:3 has been used in the study of the decomposition of off-stoichiometric Y 1:2:3, occurring on ageing within the two-phase region (Vasumathi *et al* 1990).

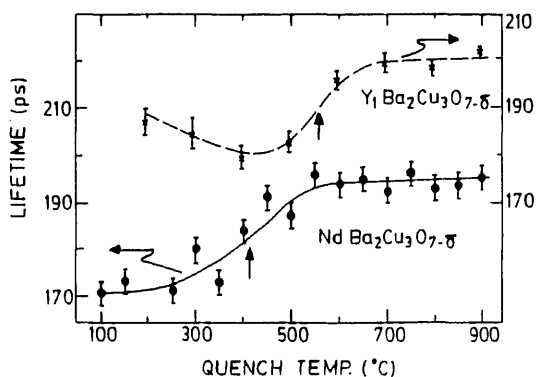


Figure 13. Variation of lifetime as a function of quench temperature in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{NdBa}_2\text{Cu}_3\text{O}_{7-x}$ (From Sundar *et al* 1991b).

Apart from the study of oxygen defects in Y 1:2:3, the intercalation of oxygen in Bi-Sr-Ca-Cu-O (Sundar *et al* 1991c) and vacancy defects in La-Sr-Cu-O (Sundar *et al* 1992) have also been investigated. The nature of flux-pinning defects that lead to an increase in critical current density on neutron and heavy-ion irradiation is a topic of considerable interest. The increase in critical current density with neutron dose has been correlated (Lu *et al* 1992) with the microvoid density as obtained by positron lifetime measurements. With the increase in realization of the importance of defects in controlling the structure and superconducting properties of HTSC materials (Jorgensen 1991), it is clear that PAS will continue to play an important role.

4.5 Fermi surface studies

One of the key issues which has a direct bearing on several theoretical models of high-temperature superconductivity has been the question of the existence of Fermi surface (Pickett *et al* 1992). Measurement of two-dimensional angular correlation of annihilation radiations (2D-ACAR), which provides information on the electron momentum distribution in solids, has been successfully applied (Berko 1983) to obtain detailed information on the Fermi surface in the A-15 superconductors. With this background, several 2D-ACAR studies have been carried out mainly on the Y 1:2:3 system (Smedskjaer and Bansil 1992; West 1992). An unequivocal answer to the question of the existence of Fermi surface was not obtained for long due to the difficulties associated with the preparation of good-quality single crystals free from defects. Recently, experiments (Haghighi *et al* 1991) on untwinned crystals have at last provided, definitive evidence for the existence of Fermi surface in good agreement with the LDA predictions (Pickett *et al* 1992). These experiments coupled with angle-resolved photoemission experiments have helped to clarify the much debated controversy with respect to the description of electronic structure of cuprates.

4.6 Fullerenes

During the last three years fullerenes, the close-caged carbon clusters C_{60} and C_{70} , have attracted considerable attention, both due to their elegant molecular symmetry and the intriguing structural, dynamic and electronic properties of their solid phase (Heiney 1992). One dominant interest in these molecular solids has been in the structural transformations with temperature and pressure which are related to the orientational correlations amongst the molecules. From the point of view of use of PAS in the study of C_{60} , it is firstly of interest to know if the positron probes the interior of the hollow cage structures or the annihilation is from the interstitial regions of the solid. From measurements (Jean *et al* 1992) of positron lifetime in C_{60} as a function of pressure (see figure 14), coupled with theoretical calculations of positron density distribution (see figure 15), it has been established that the positron probes the interstitial regions. Interesting effects of the positron dynamics between the interstices to the region within the cage structure have been seen in recent experiments (Sundar *et al* 1994) of positron lifetime vs temperature. Further, since the positron probes the interstitial region of C_{60} solid, the annihilation characteristics are sensitive to the effects of intercalation of K (Lou *et al* 1992). Interesting experiments

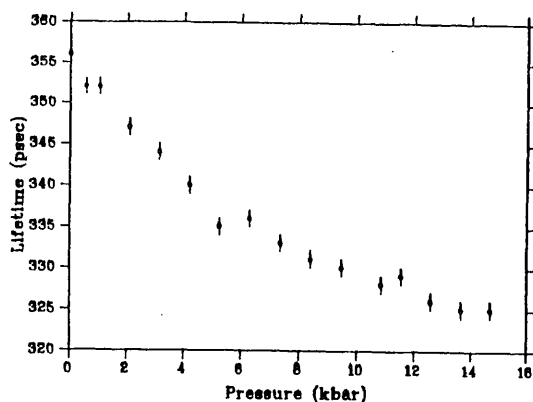


Figure 14. Positron lifetime as a function of pressure in C_{60} (From Jean *et al* 1992).

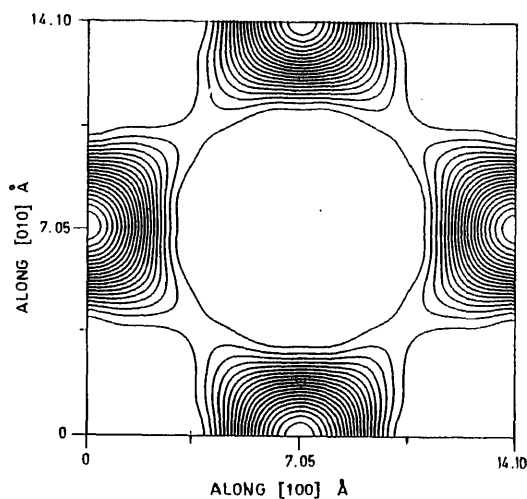


Figure 15. Positron density distribution in the basal plane of C_{60} showing the maxima in the interstitial region of the fcc lattice (From Sundar *et al* 1994).

on the decomposition of the off-stoichiometric K-doped phases, and experiments across T_c , are possible, and still remain to be done.

5. Summary and future outlook

As a result of extensive work in the last two decades, PAS is now well established as a technique for the investigation of defects in materials, in particular vacancy-type defects and small vacancy clusters. With high-resolution positron lifetime measurements, coupled with theoretical calculations, it is now possible to obtain a detailed characterization of defects. The accent in this paper has been to bring out how information related to defects is obtained in positron experiments. Further

developments will rely on the judicious application of this method to investigate interesting defect-related phenomena in materials science.

The last decade has also seen tremendous progress with respect to the developments in the technique per se. Of particular interest from the point of view of study of defects is the development of low-energy positron beam spectrometers (Mills 1983; Schultz and Lynn 1988). In contrast to the use of continuous distribution of positrons from a radioactive source, in a low-energy positron beam spectrometer, thermalized positrons emitted by the moderator such as W(110) are extracted, magnetically or electrostatically filtered, and accelerated to the few keV before impinging on the target. The use of monoenergetic positrons of tunable energy provides a method for investigation of defects in the near-surface region, at interfaces, and for depth profiling of defects (Schultz and Lynn 1988). An effort at development of a low energy positron beam spectrometer is being carried out in our laboratory (Viswanathan and Amarendra 1990). Recently, it has also become possible to obtain intense microbeams of positrons which have potential for development of positron microprobe and even positron microscopes. With these developments and an increasing realization that defects play an important role in influencing physical properties, positron studies will continue to play a crucial role in characterization of the defect properties of materials.

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Growth and characterization of some novel crystals for nonlinear optical applications

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Abstract. The advent of high intensity lasers coupled with the recent advances in crystal technology has led to rapid progress in the field of nonlinear optics. This article traces the history of materials development that has taken place over the past forty odd years and dwells on the current status in this important area. The materials aspect is discussed under three classes viz. inorganic, organic and semiorganic crystals. In the end, some of the crystal growth work that has been carried out in author's laboratory is presented.

Keywords. Nonlinear optics; polarizability; second harmonic generation; semiorganics; crystal growth.

1. Introduction

In its long history, optics, until the advent of lasers, remained linear. The tenets of linear optics are based on the assumption, valid under the first approximation, which provides the linear dependence of polarization wave generated in the medium on the interacting electromagnetic field:

$$P = \epsilon_0 \chi E. \quad (1)$$

As a result of the oscillating nature of the field associated with the radiation, the induced dipoles will oscillate and thus act as sources of radiation. When the radiation field is large, the induced polarization would become nonlinear and its dependence on the radiation field is represented by

$$P = \epsilon_0 (\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots). \quad (2)$$

An immediate consequence of this is the generation of fields at frequencies different from those of the incident radiation. For example, if the incident radiation is represented by

$$E = E_0 \cos \omega t, \quad (3)$$

then the quadratic term in E of (2) yields a component at twice the fundamental frequency, i.e.

$$E^2 = E_0^2 \cos^2 \omega t = \frac{1}{2} E_0^2 (1 + \cos(2\omega t)). \quad (4)$$

Similarly substituting (3) into (2) gives for the cubic term a component at three times the fundamental frequency. The two examples cited above are referred to as optical second and third harmonic generations respectively. In addition, there are other exotic effects such as parametric oscillation, rectification, optical phase conjugation, etc which manifest at high optical fields. However, frequency conversion is the most

studied nonlinear optical (NLO) process and is particularly important in device applications.

2. Materials perspectives

Ever since the first demonstration of second harmonic generation (SHG) in quartz (Franken *et al* 1961), progress in nonlinear optics has always been dictated by the availability of better and newer materials. The conversion efficiency of the second harmonic generation process is given by (Yariv 1985)

$$\eta_{\text{SHG}} = \frac{P_{2\omega}}{P_{\omega}} = 2 \left(\frac{\mu}{\epsilon_0} \right)^{3/2} \frac{\omega^2 d^2 l^2 \sin^2(\Delta k l / 2)}{n^3 (\Delta k l / 2)^2} \frac{P_{\omega}}{A}. \quad (5)$$

Here d is the effective nonlinear optical coefficient and k the wave vector. For a given material and for a given frequency (ω) the conversion efficiency is dependent on the square of the interaction length l , hence it is imperative that large crystals are needed. As a result of the interference from the input fundamental polarization wave and the driven harmonic polarization wave, the maximum usable length of the crystal is limited to a few microns. However, this problem could be circumvented by decreasing Δk to zero, technically known as phase matching. The quotient d^2/n^3 is called the figure of merit for SHG. This is a material-limited parameter, often meriting the first consideration, in the search for newer materials. In a chosen material and a selected interaction geometry, conversion efficiency can be further enhanced by increasing the power density (P_{ω}/A) of the input beam. This can be physically achieved by focusing the beam into the crystal, increasing the power densities to the tolerance limit, called the damage threshold.

The above discussion on the parameters influencing the conversion efficiency is for plane wave approximation of the incident beam and is valid essentially when the crystal acceptance widths are much broader than those of the laser beam. A more detailed consideration of the beam and crystal parameters gives the phase mismatching parameter ΔS as (Lin 1988),

$$\Delta S = K_1(\Delta\theta.L) + K_2(\Delta T.L) + K_3(\Delta\lambda.L), \quad (6)$$

where $(\Delta\theta.L)$, $(\Delta T.L)$ and $(\Delta\lambda.L)$ are defined as the angular, temperature and spectral bandwidths respectively, of the crystal. Hence it is essential that the temperature and spectral bandwidths are also considered while opting for a crystal for an NLO device.

In addition to the above parameters, a few other physical properties of the crystals need to be considered. For example, the chosen material should have large transparency window, high melting point, mechanical stability and chemical inertness. There are very few materials which satisfy most of these requirements. Hence the search for new materials seems to be unending. Though other forms of materials, like thin films, polymers, etc. are also currently being explored, the discussion herein is limited to single crystals.

Table 1. Some physicochemical properties of inorganic NLO materials.

Material	LiNbO ₃	KD*P	LiIO ₃	β -BaB ₂ O ₄	KTP	LiB ₃ O ₅	KNbO ₃
Point group	3 m	42 m	6 m	3 m	mm 2	mm 2	mm 2
Transparency (nm)	350–5000	180–1800	340–4000	198–2600	350–4500	160–2300	400–5500
Refractive indices at 1064 nm	$n_o = 2.2322$ $n_e = 2.1560$	$n_o = 1.4931$ $n_e = 1.4582$	$n_o = 1.8567$ $n_e = 1.7168$	$n_o = 1.6551$ $n_e = 1.5425$	$n_x = 1.5737$ $n_y = 1.7395$ $n_z = 1.8305$	$n_x = 1.5649$ $n_y = 1.5907$ $n_z = 1.6052$	$n_x = 2.1194$ $n_y = 2.2195$ $n_z = 2.2576$
d_{eff} (pm/V)	5.1	0.35	1.8	1.6	3.2	0.85	13
Threshold power (MW)	0.70	30	66	13	0.029	NA	NA
Damage threshold (GW/cm ²)	0.3 (10 nsec)	5 (1 nsec)	1 (0.1 nsec)	23 (14 nsec)	9–20 (1 nsec)	1–4 (12 nsec)	1 (10 nsec)

NA, Not available

2.1 Inorganic crystals

In the initial stages, the materials explored for nonlinear optical applications had always been inorganic. Many inorganic crystals are well studied in terms of their physical properties. Since these materials are mostly ionic bonded, it is always easier to synthesize inorganic materials. Often these have high melting points and high degree of chemical inertness. High-temperature oxide materials are well studied for diverse applications like piezoelectricity, ferroelectricity, pyroelectricity and electro-optics. Hence when the search for new materials began in NLO, scientists often trusted their intuition, screened the known materials, and were fairly successful. Some of the most useful crystals discovered are LiNbO_3 , KNbO_3 , potassium dihydrogen phosphate (KDP) and its analogues, potassium titanyl phosphate and its analogues, beta barium borate, etc. Indeed most of the commercial frequency doublers used presently are all made of these inorganic materials. Table 1 summarizes the present status of these materials, comparing all the device-related parameters. However, as early as 1969, Bergman *et al* (1969) indicated that inorganic materials have only $\approx 20\%$ probability of acentricity. Hence in the search for newer materials with higher nonlinearity, inorganics stand a poor chance and the advances have been limited in the past two decades.

2.2 Organic materials

Organic compounds are often formed by weak van der Waals and hydrogen bonds and hence possess high degree of delocalization. Thus they are expected to be optically more nonlinear than inorganic compounds. Some of the advantages of organic materials include ease of varied synthesis, scope for altering the properties by functional substitutions, inherently high nonlinearity, high damage resistance, etc. The prototype organic NLO material contains one or more delocalized bonds, typically a ring structure like benzene. When substituted with donor and acceptor

Table 2. Some physicochemical properties of organic NLO materials.

Material	MNA	POM	DAN	MMONS	MBANP	MAP
Point group	mm 2	222	2	mm 2	2	2
Melting point ($^{\circ}\text{C}$)	114	136	166	NA	84	80.9
Transparency (nm)	480–2000	500–1700	485–2700	510–2100	NA	500–2500
Refractive indices at 1064 nm	$n_x = 1.800$ $n_y = 1.600$ $n_z = ?$	1.663 1.829 1.625	1.517 1.636 1.843	1.530 1.630 1.961	1.650 1.714 1.688	1.507 1.59 1.843
Nonlinear coefficient ($\times 10^{-9}$ esu)	$d_{11} = 60$ $d_{12} = 90$	$d_{14} = 23$ $d_{25} = 23$ $d_{36} = 23$	$d_{22} = 12.4$ $d_{23} = 119$	$d_{24} = 55$ $d_{32} = 41$ $d_{33} = 184$	$d_{22} = 8.3$	$d_{21} = 40$ $d_{22} = 44$ $d_{23} = 8.8$
Damage threshold (GW/cm^2)	0.2 (20 n sec)	2 (0.02 n sec)	5 (10 n sec)	NA	1 (12 n sec)	3 (10 n sec)

MNA: 2-methyl-4-nitroaniline; POM: 3-methyl-4-nitropyridine-1-oxide; DAN: 4-(N,N-dimethylamino)-3-acetamido nitrobenzene; MMONS: 3-methyl-4-methoxy-4'-nitrostilbene; MBANP: 2-(α -methylbenzyl-amino)-5-nitropyridine; MAP: methyl-(2,4-dinitrophenyl)-amino-2-propanate.

Table 3. Some physicochemical properties of semiorganic NLO materials*.

Material	dLAP	BTCC	ZTS	ATCC	ATMB	TSCCB
Point group	2	mm 2	mm 2	3 m	3 m	m
Melting point (°C)	130	185	> 200	101	138	230
Transparency (nm)	250–1300	300–2000	300–2000	300–1500	330–1500	330–1420
Refractive indices	$n_x = 1.49769$ $n_y = 1.5595$ $n_z = 1.5686$	$n_x = 1.6097$ $n_y = 1.7902$ $n_z = 1.8600$	$n_x = 1.6306$ $n_y = 1.6936$ $n_z = 1.6984$	$n_0 = 1.6996$ $n_e = 1.6400$	$n_0 = 1.7046$ $n_e = 1.6341$	$n_x = 1.7200$ $n_y = 1.7180$ $n_z = 1.8120$
Nonlinear susceptibility ($\times 10^{-9}$ esu)	$d_{14} = 0.22$ $d_{16} = 0.48$ $d_{22} = 0.68$	$d_{31} = 2.75$ $d_{32} = 0.2$ $d_{33} = 2.7$	$d_{31} = 0.31$ $d_{32} = 0.35$ $d_{33} = 0.23$	$d_{31} = 1.5$ $d_{22} = 0.7$ $d_{33} = 1.9$	$d_{31} = 0.27$ $d_{22} = 8.2$ $d_{33} = 2.7$	$d_{11} = 0.5$ $d_{13} = 0.3$ $d_{15} = 2.8$
d_{eff} (pm/V)	0.98	1.65	0.13	NA	NA	0.9
Damage threshold (GW/cm ²)	13.0 (1 n sec)	32 (32 p sec)	40 (32 p sec)	0.32 (40 n sec)	NA	NA

* Literature values, some of them redetermined during the present investigation.

BTCC: Bis(thiourea) cadmium chloride; ATCC: triallyl thiourea cadmium chloride; ATMB: Triallyl thiourea mercury bromide; TSCCB: thiosemicarbazide cadmium bromide.

at the *para* position, (e.g. *p*-nitroaniline) they have large induced dipole moments under the influence of electromagnetic fields. However, such structures, when packed as crystals, tend to be mostly centrosymmetric, thus leading to vanishing dipole moment. A suitable addition at another site, as in the case of 3-methyl 4-nitroaniline, can ensure a macroscopically non-vanishing dipole moment for the donor-acceptor-substituted systems. The above example typifies the strategy of molecular engineering towards achieving efficient nonlinear materials (Chemla and Zyss 1987). Table 2 gives the list of well-developed organic NLO materials and their physical properties. However, there has been little progress in fabricating devices out of these molecular crystals. These crystals have several unfavourable physical parameters. Large dipole moment which leads to the large $\chi^{(2)}$ is also responsible for increased absorption at higher frequencies. Hence most of these molecular materials have poor transparency and small transparency windows. Consequently, the generated harmonic wave gets absorbed in the crystal, leading to poor efficiency. Also, organic NLO materials are inherently poor in mechanical hardness, and have low melting points and poor chemical inertness. Owing to the high polar nature of the molecules they often tend to crystallize as long needles or thin platelets.

2.3 Semiorganic materials

The inherent limitation on the maximum attainable nonlinearity in inorganic materials and the moderate success in growing device-grade organic single crystals have made scientists adopt newer strategies. The obvious one was to develop hybrid inorganic-organic materials with little trade-off in their respective advantages. This new class of materials has come to be known as the semiorganics (Newman *et al* 1990). One approach to high-efficiency, optical-quality organic-based NLO materials in this class is to form compounds in which a polarizable organic molecule is stoichiometrically bonded to an inorganic host. A typical case is the formation of inorganic salts of chiral organic molecules (classified as type I). L-Arginine phosphate monohydrate (LAP) is an example of this class. The choice of organic molecules to form salts are plenty. For example tartrates, oxalates and amino acid salts are predominantly NLO-active.

An alternate approach is to form metal coordination complexes of organic materials (type II). The choices for ligands in type II are unlimited. In fact, the organic part need not be noncentrosymmetric. This is typified by the example of thiourea, which forms excellent complexes with Zn, Cd and Hg. Thiourea is more polarizable than urea because of the presence of large sulphur atoms and the hydrogen bonds in NH_2 ensure the lack of centre of inversion in many thiourea complexes. The other popular choices for ligands in type II are allylthiourea, guanidium and dithiocarbamate.

An added advantage of this class of materials is that they have moderate nonresonant $\chi^{(3)}$ which can be resonantly enhanced by doping with metals that can absorb in the operable wavelength. For example, zinc tris (thiourea) sulphate (ZTS) has a $\chi^{(3)}$ value 0.1 times that of CS_2 which can be enhanced to 1.5 times CS_2 by doping it with Co at 10 ppm (Newman *et al* 1990). Table 3 gives a list of some of the semiorganic compounds and their physical properties.

of crystals, LAP and its deuterated analogue dLAP, ZTS, BTCC, 3-methoxy-4-hydroxybenzaldehyde (MHBA) (all grown from solution), LiNbO_3 and potassium titanyl phosphate (KTP). For want of space detailed account of the investigations carried out on them will not be given here. Below we describe only the growth aspects of some of these crystals.

3.1 Lithium niobate

Lithium niobate (LiNbO_3) continues to be one of the technologically important materials because of its diverse applications (INSPEC 1989; Prokhorov and Kuzminov 1990). The increasing applications of LiNbO_3 crystals with more and more stringent specifications have required continued studies on the growth and characterization of this crystal. High-quality LiNbO_3 crystals are grown by the Czochralski technique.

In our case LiNbO_3 was synthesized from Li_2CO_3 and Nb_2O_5 . The congruent composition (Li_2CO_3 48.45 mole%) was prepared through solid-state reaction in a platinum crucible. Autox oxide puller, custom built to grow oxide crystal boules of 25 mm diameter by Cambridge Instruments, England, was employed in the growth experiments. Seed crystals were prepared from *c*-axis-grown LiNbO_3 boule. The charge was contained in a platinum crucible of dimensions 50 mm diameter, 50 mm height and 1.5 mm wall-thickness. The platinum crucible was surrounded by a magnesia crucible as a support. An inverted magnesia crucible with a suitable viewing slot and a hole at the top to allow the pull rod to pass through was used as an after-heater.

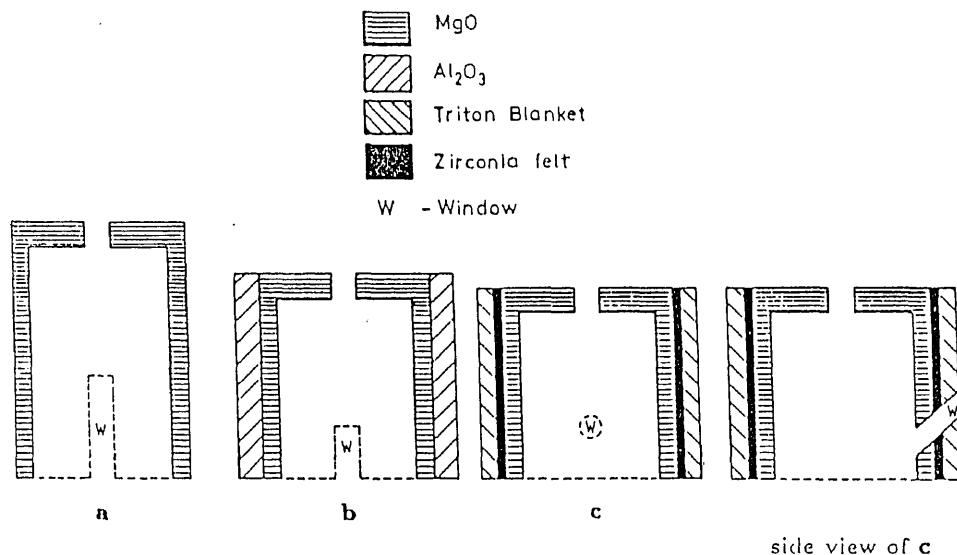


Figure 1. Systematic improvements in after-heater configurations.

The entire assembly was surrounded by a 'Y'-type quartz tube inside which an $O_2 + Ar$ atmosphere was maintained. The charge was melted by an RF heating system.

One of our important objectives here was to see whether the diameter of the crystal boule could be increased. As was mentioned earlier, the puller used was designed for growing 25 mm diameter crystals. The systematic effort on the improvement of the after-heater configuration enabled us to grow routinely 32 mm diameter crystals. Increase of the diameter from 25 mm to 32 mm corresponds to 45% increase in the yield by weight and an achievement of crystal to crucible diameter ratio of 64%. The various stages of improvement in the after-heater configuration which led to this achievement are schematically shown in figure 1. The improvement here is essentially in terms of reducing the heat loss and achieving less sharper temperature gradient. The configuration shown in figure 1c has considerably less heat loss through the window and by radiation thereby improving the thermal conditions.

In most cases the crystals were found to be colourless, though at times the crystals grown were with a slight yellowish tinge. The coloured crystals were annealed at about $1000^\circ C$ in oxygen atmosphere for two days. After this the temperature was brought down to $300^\circ C$ at a rate of $25^\circ C/h$ and then the furnace was switched off. The annealing procedure not only makes the crystal colourless, but also removes thermal stress, if any, present in the crystal. Figure 2 shows two *c* cut wafers of $LiNbO_3$ which clearly show the improvement in terms of diameter.

To study the domain structure, polished *c* cut crystals were etched in HF and HNO_3 in 1:2 ratio at about $100^\circ C$ for 30 to 45 min in a temperature-controlled bath. The difference in the etching rate between the positive and negative domains was observed with a polarizing microscope. Figure 3a shows a typical domain pattern in unpoled $LiNbO_3$. In order to monodomainize the crystal, blocks cut perpendicular to *c*-axis were poled at high temperature, for which purpose platinum paste 31333 supplied by Eltech Corporation, India, was used. The crystal coated with the platinum paste was kept in between two platinum plates, from which platinum wires were taken out. The whole assembly was kept in the uniform temperature region of a Stanton Redcraft tubular furnace controlled by a temperature programmer/controller.

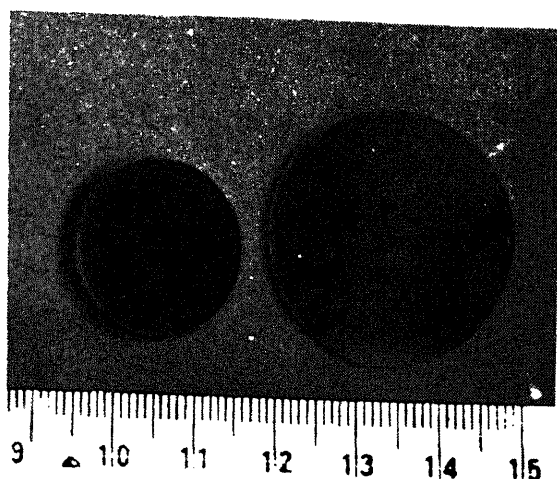


Figure 2. $LiNbO_3$ wafers showing improvement in boule diameter.

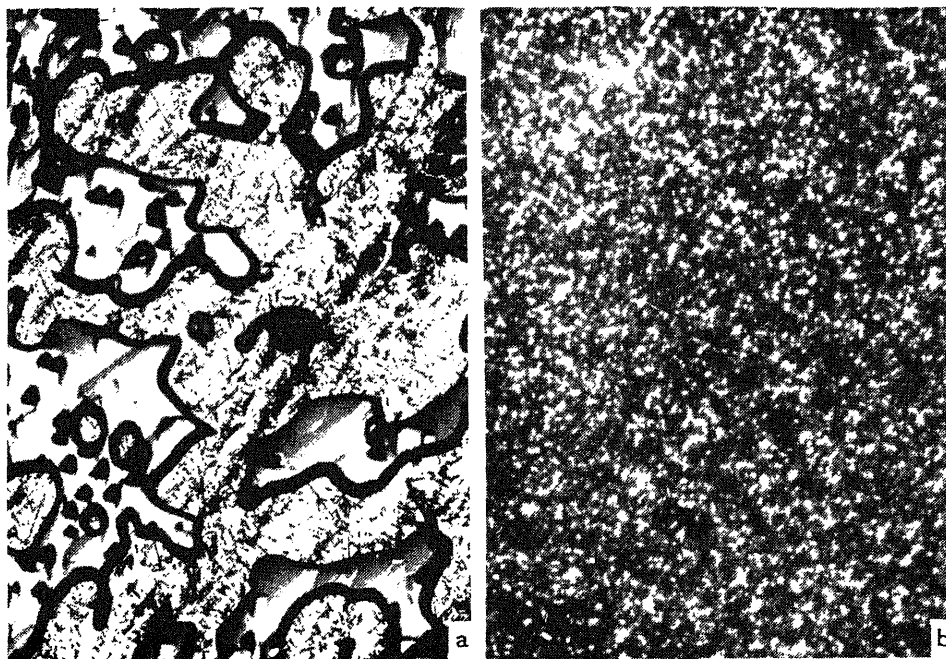


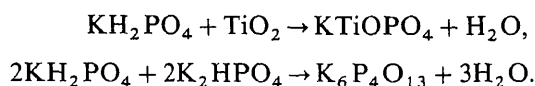
Figure 3. Domain patterns in (a) unpoled LiNbO₃ and (b) poled LiNbO₃ crystal (showing positive domain) ($\times 75$).

The crystal was heated to 1200°C at a rate of 5°C/min. A 2 mA/cm² dc current was passed through the crystal using a Keithly constant-current source. It was cooled slowly at a rate of 20°C/h up to 1000°C with polarizing current and then at a rate of 100°C/h to room temperature. The crystal was removed from the furnace at room temperature. After lightly polishing the crystal it was etched again in HF and HNO₃ in 1:2 ratio. Figure 3b shows the domain structure on the positive face of the crystal. As can be seen from the figure, the resulting crystal boule is of single domain nature.

3.2 Potassium titanyl phosphate

Potassium titanyl phosphate (KTiOPO₄) commonly known as KTP, is a well-known nonlinear optical material frequently used for frequency doubling of Nd-doped lasers (Zumsteg *et al* 1976). It is also an excellent electrooptic and waveguide material, making it an ideal candidate in integrated optical applications (Bierlin and Arweiler 1986).

In our laboratory, KTP crystals are grown from potassium phosphate (K₆P₄O₁₃) flux by self-nucleation employing slow cooling. The ingredients were KH₂PO₄ (AR grade), TiO₂ (GR grade) and K₂O₄ (AR grade). KTiOPO₄ and K₆P₄O₁₃ are obtained by the *in situ* reaction as follows:



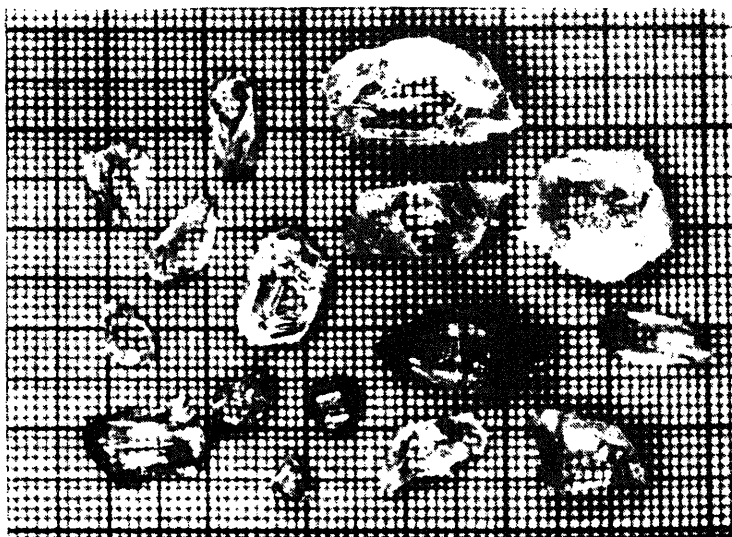


Figure 4. Typical KTP crystals grown from flux.

The ingredients were taken in a platinum crucible and kept at 1050°C for homogenization. After two days of homogenization the temperature was brought down to saturation temperature (i.e. 975°C) and slow cooling was started. Different cooling rates and different termination temperatures (temperature at which the furnace power was switched off) were used. After the completion of programmed cooling, the furnace was allowed to reach room temperature by natural cooling after which the crucible was taken out and the flux was dissolved in hot water to harvest the crystals. Figure 4 shows typical KTP crystals grown in the laboratory. The crystals selected for microtopographical observation were cleaned thoroughly with hot water using a fine brush. The crystal habit faces were viewed under a Leitz Orthoplan polarizing microscope in reflection mode.

Interesting dendritic structures were obtained on the habit faces which mainly depend on the cooling rates. For example the habit faces of crystals grown under very fast cooling rates (say $1\text{--}2^{\circ}\text{C/h}$) exhibited highly coarse dendritic structures. As cooling rate is lowered the dendritic structure becomes finer in nature and dendritic density also decreases. Under very low cooling rates (say 2°C/day) smooth stepped surfaces without any dendrites could be obtained. These dendritic structures are formed because of the rapid increase in supersaturation during the final stages of growth, i.e. when the flux is approaching the solidification temperature. The underlying step pattern on the (100) habit faces is a clear manifestation of two-dimensional layer growth mechanism operating in the growth of these crystals. The details of these studies have already been published (Dhanaraj and Bhat 1990).

Recently we have made considerable progress in growing these crystals by top-seeded solution growth technique, for which purpose the required facility has been indigenously fabricated. Currently efforts are on in optimizing the growth conditions (Satyanarayan and Bhat 1993).

3.3 3-Methoxy-4-hydroxybenzaldehyde

3-Methoxy-4-hydroxybenzaldehyde (MHBA), is an efficient molecular nonlinear optical material. This has relatively weak donor and acceptor ($-\text{CHO}$ and $-\text{OH}$) at *para* positions in a benzene ring and $-\text{OCH}_3$ group attached at the *meta* position, ensuring an acentric crystal structure. Its powder SHG efficiency is as high as 30 times that of urea and it has transparency down to 362 nm (Yakovlov and Poezzhalov 1991; Tao *et al* 1992; Zhang *et al* 1993). A combination of these properties makes MHBA an excellent material for investigation as a potential frequency doubler for GaAs lasers, useful in high-storage-density optical memories.

3.3a Growth from solution: Earlier workers have grown crystals of MHBA from different solvents (Singh *et al* 1991; Tao *et al* 1992; Zhang *et al* 1992). Since we found out that most of the attempted solvents (water, methanol, chloroform, acetic acid) were not very suitable for crystal growth of MHBA, we tried mixtures of these solvents in different proportions. Crystals large enough for characterization were obtained from either a mixture of acetic acid and water or chloroform and acetone and are shown in figure 5. Though the mixture of acetic acid and water gave larger crystals, under the prolonged growth durations required for achieving this the solution turned deep yellowish in colour. We found that for better optical-quality crystals, a mixture of chloroform and acetone is more suitable. A summary highlighting the extremes of the results obtained in some solvent mixtures is presented in table 4. MHBA grows as rods and needles from many of the solvents and solvent mixtures (not listed here). This is due to the fact that the molecules align easily head-to-tail forming hydrogen bonds with the solvent molecules.

3.3b Growth from melt: It has been reported that the melting point of MHBA is 82°C and the compound does not undergo any phase transition till that temperature (Zhang *et al* 1992). Differential scanning calorimetry carried out by us indicated that

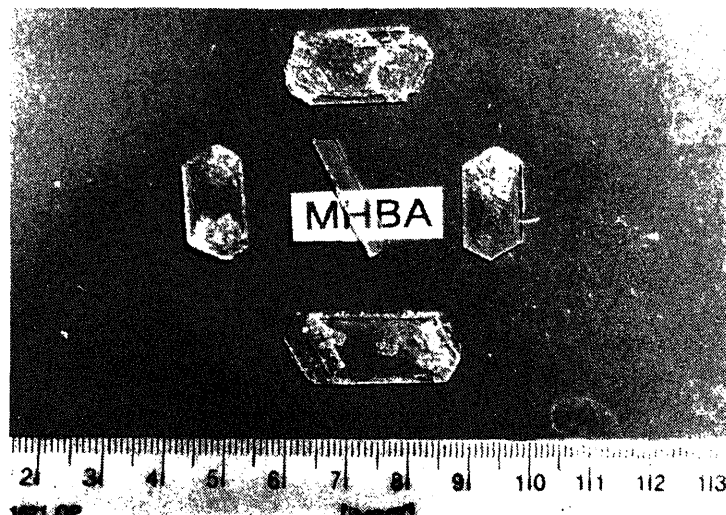


Figure 5. MHBA crystal grown from chloroform–acetone mixture.

Acetic acid + water (2:1)	40.9	Plates	Good
Acetic acid + water (1:1)	28.4	Prisms	Good
Acetic acid + water (1:2)	14.59	Plates	Good
Chloroform + acetone (1:1)	73.72	Plates	Very good
Chloroform + acetic acid (1:1)	32.02	Prisms	Good

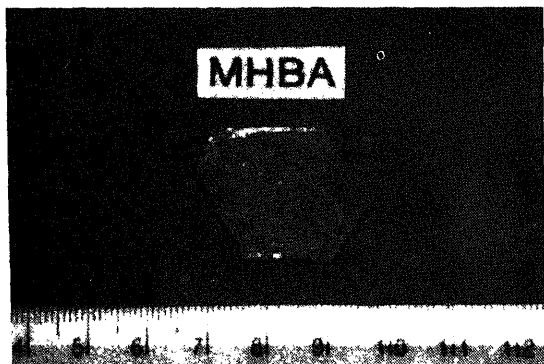
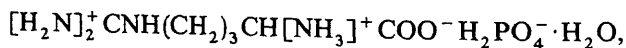


Figure 6. An MHBA crystal grown from undercooled melt.

the compound melts at 82°C, solidifies below 50°C, and does not decompose till 90°C. Hence attempts were made to grow crystals from the undercooled melt (Venkataramanan *et al* 1994a). The material was taken in a 250 ml flask and melted at 82.5°C. The charge was then slowly cooled down to 81°C to supercool it by 1.5°C. A seed crystal grown by spontaneous nucleation was carefully lowered into the melt and made to grow by release of latent heat of crystallization. Crystals of size 30 × 20 × 2 mm³ were grown in 6 h (figure 6). The grown crystals were polymorphic in habit and had good transparency. Further, unlike solution-grown crystals, these crystals did not suffer from inclusions and their preferential incorporation into certain regions. From this point of view, the melt growth is more suitable for growing MHBA crystals.

3.4 LAP and dLAP

L-Arginine phosphate monohydrate (generally known as LAP), with chemical formula



is one of the new type I semiorganic nonlinear optical materials. Compared to KDP, LAP is nearly three times more nonlinear, is more angularly sensitive, has a damage threshold 2 to 3 times higher, and is less deliquescent (Eimerl *et al* 1989; Sasaki *et al*

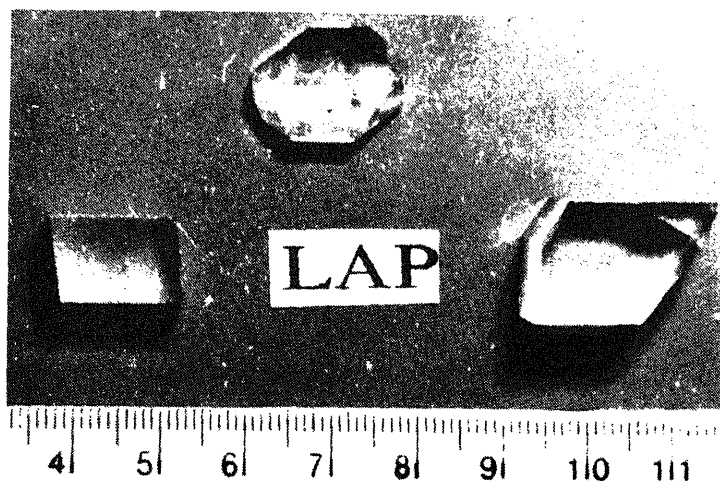


Figure 7. Typical LAP crystals grown.

1989; Yokatani *et al* 1989). It crystallizes in monoclinic structure with space group $P2_1$ and is optically biaxial (Aoki *et al* 1971). LAP has an absorption band around the Nd:YAG laser fundamental which can be red-shifted by deuterating it. Hence dLAP has an added advantage for frequency conversion applications of Nd lasers. LAP crystals are grown in our laboratory from aqueous solutions by slow cooling as well as by slow evaporation. The problems associated with growth of LAP, like microbial growth and colouration of the solution, have been investigated and the details have been published elsewhere (Dhanaraj *et al* 1991). Large LAP crystals are grown by slow cooling from 45°C to 30°C at the rate of 0.2°C to 0.5°C per day (figure 7). The ideal morphology of LAP and its variations under different growth conditions (pH and colouration of the solution) have already been reported by us (Dhanaraj *et al* 1991).

Deuterated LAP is synthesized in a glove box in N_2 atmosphere using D_2O , P_2O_5 and L-arginine. Seed crystals of dLAP are prepared by spontaneous nucleation in a sealed flask by slow cooling. Growth of dLAP is carried out in a closed flask with a *n*-hexane layer on the surface of the solution. Slow cooling is carried out from 35°C to 20°C at a rate of 0.5°C a day. Crystals up to $13 \times 10 \times 8 \text{ mm}^3$ could be grown in 100 ml solution. Figure 8 shows a photograph of typical dLAP crystals. The morphology of these crystals is quite similar to that of LAP (Venkataramanan *et al* 1994b).

The prominent microbial species identified in LAP solutions are of *Aspergillus* family. Most of the microbes that grow in LAP were found to be aerobic. A layer of immiscible liquid over the growth solution can isolate the solution from the atmosphere, thereby preventing microbial growth. We covered sterilized LAP solution with a thick layer of *n*-hexane and were able to alleviate the problem (Dhanaraj *et al* 1991).

A recent experiment on KDP growth (Wang *et al* 1992) has revealed that addition of droplets of mercury to the growth solution reduces microbial growth. We also found that addition of Hg in the LAP solution delays the appearance of microbial colonies, if not completely eliminate it. However, from our experience, the technique

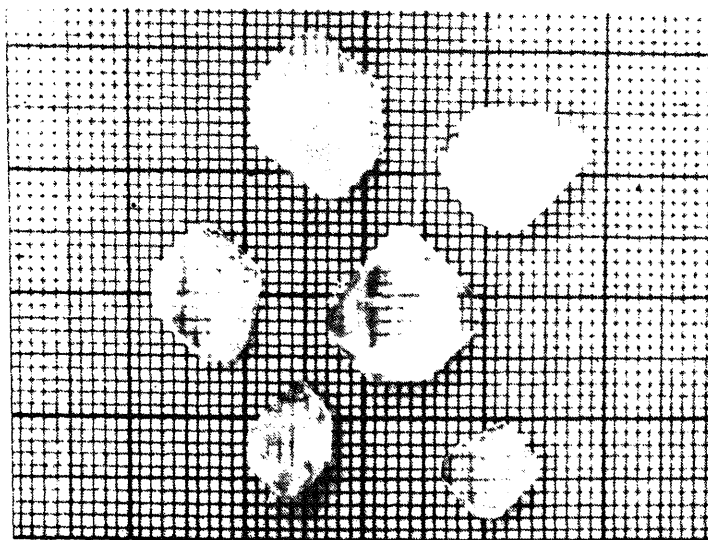
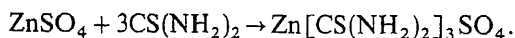


Figure 8. Typical dLAP crystals grown.

of covering the sterilized solution with a thick layer of immiscible liquid seems to be the most effective method to prevent microbial growth for extended periods. The problem of microbial growth and the influence of pH, Hg and a layer of *n*-hexane were common for both LAP and dLAP.

3.5 Zinc tris(thiourea) sulphate

Zinc tris(thiourea) sulphate (ZTS) is a recently developed type II semiorganic nonlinear crystal (Marcy *et al* 1992). It is a good example of NLO material in which large nonlinearity of a π conjugate organic material is combined with favourable crystal growth behaviour and mechanical properties. As a first step ZTS was synthesized from ZnSO_4 and thiourea following the reaction



The mixture had to be stirred vigorously to avoid precipitation of other phases. The resultant precipitate of ZTS was dried and weighed to measure the yield. The product was further purified by repeated recrystallization from hot water. Thiourea has the coordinating capacity to form a variety of zinc–thiourea complexes. To ensure purity of yield, a powder X-ray diffractogram was taken after every synthesis and analysed for mixed phases.

Since no solubility data were available in the literature for ZTS, efforts were made to measure the solubility in water. Solubility was measured from 30°C to 80°C in steps of 5°C or less. The resultant data could be fitted to a curve following the equation

$$S = at^2 + bt + c,$$

where S is the solubility expressed in g/100 ml and t the temperature in °C. The

constants evaluated were $a = 9.979 \times 10^{-4}$, $b = -0.0055$ and $c = 4.6879$. Figure 9 is the solubility curve for ZTS. It can be seen from the curve that though there is a positive slope, the variation of solubility with temperature is quite low. This proved to be a serious handicap in growing large crystals by slow cooling and hence solvent evaporation was adopted as the technique to grow the crystals. Subsequently, single crystals of ZTS were grown from aqueous solution by evaporation at room temperature. Crystals up to $25 \times 12 \times 3 \text{ mm}^3$ could be grown without seeding in about two weeks time. The crystals grown by spontaneous nucleation were optically transparent and free from visible inclusions. They were generally platy with the prominent face containing $[100]$ plane. Good optical-quality crystals as large as $24 \times 18 \times 16 \text{ mm}^3$ were grown subsequently by seeding the saturated solution and by evaporation of solvent (figure 10). The crystals were nonhygroscopic and optically transparent. Further work is in progress.

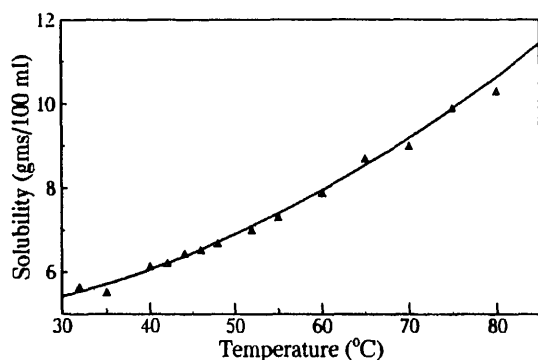


Figure 9. Solubility curve for ZTS with water as solvent.

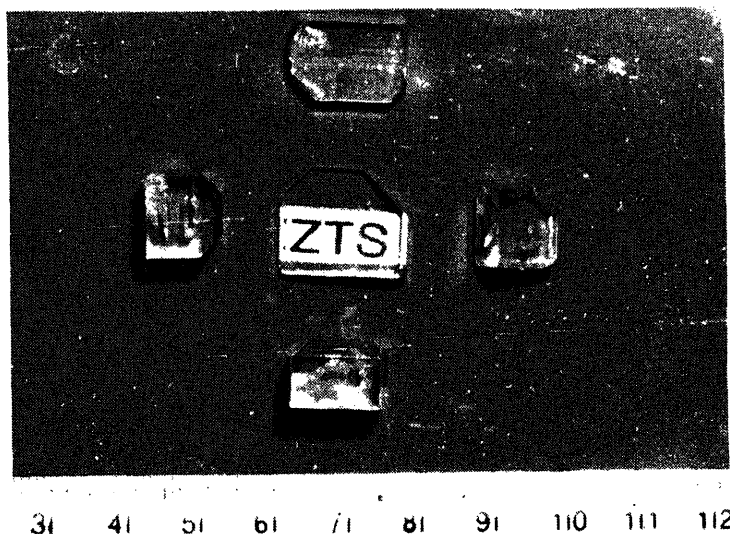


Figure 10. Optical-quality ZTS crystals.

4. Conclusions

In this review we have briefly discussed nonlinear optical crystals from the materials points of view. Initially an elementary introduction to nonlinear optical phenomena with emphasis on second harmonic generation was given. The material parameters to be optimized for maximizing SHG efficiency were then highlighted. The present status of three classes of NLO materials, viz. inorganics, organics and semiorganics, has been summarized. A brief account of crystal growth experiments carried out in the author's laboratory on some typical crystals belonging to each of the above class is given.

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Grain-boundary scattering in semiconductor films

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Abstract. Alternative technique for studying grain-boundary scattering phenomena in high-resistivity semiconducting films has been indicated. The combined effect of the presence of electric field and mechanical stress at the grain boundaries was considered. It is shown that the grain boundary potential, density of trap states, and carrier concentration of the films can be obtained by measuring reflectances of the films deposited on non-absorbing substrates.

Keywords. Grain-boundary scattering; semiconductor; polycrystalline film; Franz–Keldysh effect.

1. Introduction

Most of the devices based on compound semiconductors are generally polycrystalline in nature where the films are composed of a large number of crystallites joined together by grain boundaries. The intercrystalline boundaries or grain boundaries are one of the most dominant factors controlling conduction mechanism in polycrystalline semiconductor films. In electronic devices and solar cells based either on elemental or compound semiconductors, the deleterious effects of grain boundaries are well known. Several models have been proposed by workers in this field to describe grain-boundary phenomena in polycrystalline films (Volger 1950; Kamins 1971; Seto 1975, 1976; Baccarani *et al* 1978). All the methods involved measuring either electrical conductivity (σ) or Hall mobility (μ) at lower temperatures, when the contributions due to phonons to the total scattering is less. However, it is seen that the films used for device fabrication are generally of high resistivity and as such measurement of σ and specially μ becomes difficult, if not impossible, at lower temperatures. So there is a need for an alternative route for studying the grain-boundary effect in highly resistive films. Measurements of optical reflectances have offered such a possibility.

The effect of grain boundaries with an inherent space charge region due to the interface results in band bending. This is reflected in the departure from the sharpness of the fall of absorption coefficient (α) near the absorption edge. This culminates in the appearance of an additional absorption at longer wavelength. The amount of additional absorption depends on the grain size of the film.

The effects of grain boundaries on the electronic structure and optical properties of a polycrystalline semiconductor are mainly determined by the following three factors:

(i) Physicochemical imperfections: They arise from atomic bond angle and bond length deviations.

(ii) Geometrical imperfections: (a) External electric fields arising as a result of the screening of the charge near the grain-boundary region, and (b) the presence of mechanical stresses due to structural defects and dislocations at the grain-boundary regions.

However, for polycrystalline films with moderate grain size, the contribution of the physicochemical imperfections to the grain-boundary effect is quite negligible (Gavrilenko 1987). In this case, geometrical imperfections mainly govern the electronic and optical properties. Several attempts (Redfield 1963; Dow and Redfield 1970; Bujatti and Marcelja 1972; Bugnet 1974; Szczyrbowsky and Czapla 1977) were made to describe the optical absorption in polycrystalline films. Among them, the Dow-Redfield model (Redfield 1963, 1965; Dow and Redfield 1970, 1972), which assumes that the excess absorption is due to Franz-Keldysh effect arising out of the electric field present in the material, seems to be a realistic approach towards understanding the absorption behaviour at the band edge due to grain boundaries. We present here a modified treatment for evaluating the grain-boundary scattering effects in polycrystalline films as presented by Dow-Redfield by considering the effects of surface roughness that may prejudice the determination of the absorption coefficient in polycrystalline films (Bhattacharyya *et al* 1992a,b). We also considered the effect of mechanical stress present at the grain boundaries on the absorption coefficient for the above films. The experimental data were fitted by considering all the possibilities to find out conditions of the best fit. This method allows one to evaluate the grain-boundary barrier height (E_b), density of trap states (Q_t) and carrier concentration (N_d) in high-resistivity films where determination of the above quantities by conventional techniques is extremely difficult.

2. Theory

2.1 Franz-Keldysh effect

The band bending near the absorption edge and the broadening of the tail end of the absorption spectrum ($\alpha - h\nu$ plot) of polycrystalline semiconductor films mainly arise out of the contributions from three different phenomena: band-to-band absorption beyond the fundamental band edge, defect and impurity absorption, and an excess absorption caused by the Franz-Keldysh effect arising out of the built-in electric field in the material. The Franz-Keldysh effect is basically phonon-assisted tunnelling which considers that in the presence of an electric field the electron has a non-zero probability of being in the forbidden gap. This allows a photon to cause a transition to the conduction band at energies less than the bandgap (E_g). Based on this basic assumption, Dow and Redfield (1970, 1972) obtained an expression for α containing the field (F) and the expression was subsequently modified by Bujatti and Marcelja (1972) and Bugnet (1974).

Bujatti and Marcelja modified the Dow-Redfield model by assuming spherical crystallites with some distribution $P(R)$ of the radius (R) of the spheres. They could obtain a useful expression for the normalized total absorption (A) from which the potential barriers at the grain boundaries could be obtained under some simplified assumptions concerning the shape of the barrier. Using the subscript zero to indicate quantities at the energy gap, the normalized total absorption was expressed as (Bujatti

and Marcelja 1972)

$$A/A_0 = \frac{\int_0^\infty P(R) dR \int_0^R \alpha^E(F, \hbar\omega) r^2 dr}{\int_0^\infty P(R) dR \int_0^R \alpha_0^E r^2 dr}, \quad (1)$$

where $P(R)$ is the probability for a crystallite to have a radius R . It can be noted here that α appearing in (1) is a function of both photon energy and electric field in the crystallites. $\alpha^E(F, \hbar\omega)$ may be expressed in its generalized form as

$$\alpha^E(F, \hbar\omega) = I(F, \hbar\omega) F^{1/3}, \quad (2)$$

with

$$I(F, \hbar\omega) = K \omega^{-1} \int_y^\infty A_i^2(z) dz, \quad (3)$$

$$K = \frac{4\mu e^4 |\langle P^2 \rangle|}{m_0^2 \hbar^2 n \varepsilon_0 c} \gamma^{1/3}, \quad (3)$$

$$|\langle P^2 \rangle| = \frac{m_0 E_g (E_g + \Delta_0)}{12(E_g + 2\Delta_0/3)} \left(\frac{m_0}{m_e} - 1 \right), \quad (4)$$

$$\mu = [m_e m_h / (m_e + m_h)]; \quad \gamma = (2\mu/\hbar^2),$$

and

$$y = \gamma^{1/3} F^{-2/3} (E_g - \hbar\nu).$$

Here m_0 , m_e and m_h are the free and effective masses of electron and hole respectively, Δ_0 the spin-orbit splitting, n the refractive index, and c the velocity of light. The subscript zero indicates quantities at the energy gap (E_g). ε_0 is the permittivity of free space.

For polycrystalline films with large crystallites, the surface states are, in general, all occupied by electrons and the electric field close to the surface of the grains decays exponentially as shown in figure 1. We assumed here a field distribution in the

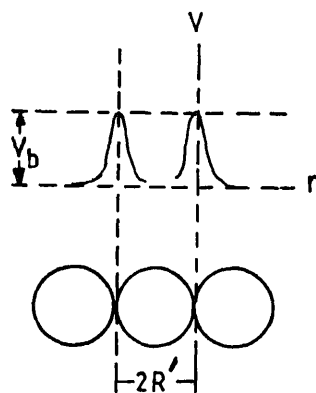


Figure 1. Potential form at the grain boundaries with different grain size.

following form:

$$F = F_s \exp[-k(R-r)], \quad (5)$$

where $F_s (= \frac{e^2 Q_t}{\epsilon})$ is the ratio of surface charge density and static dielectric constant, $k [= \{(4\pi e k_b T)/N_d e^2\}^{-1/2}]$ the inverse of the Debye screening length (λ_d), Q_t the density of trap states at the grain boundaries, and N_d the carrier concentration. This form of field distribution is a generalized one which can describe both partially and fully depleted conditions of the grains (Bhattacharyya *et al* 1993). The depletion at the grain-boundary regions results in band bending and consequently in optical absorption below the band-edge region. In order to include the contribution of different grain sizes in α , we have assumed a distribution of grain size having spherical nature of the form given by (Bhattacharyya *et al* 1992b)

$$P(R) = (R - R_{\min})(R_{\max} - R) \exp(-R^2/\delta^2), \quad (6)$$

where $R_{\max} = \bar{R} + \delta$ and $R_{\min} = \bar{R} - \delta$, $\bar{R} = (R_{\max} + R_{\min})/2$, and $\delta (= 0.76\bar{R})$ is the half-width of the distribution of R . This probability function $P(R)$ increases rapidly for small values of R and then decreases with a Gaussian tail for large values of R .

Using (2) to (6) the final form of 1 becomes:

$$A/A_0 = \alpha^E(\hbar\omega)/\alpha_0^E = (1/D) \left[\frac{\sqrt{\pi}}{12} (k\delta)^2 I_1 - (k\delta/3) I_2 + \frac{\sqrt{\pi}}{8} I_3 \right], \quad (7)$$

or

$$\alpha^E(\hbar\omega) = (\alpha_0^E/D) \left[\frac{\sqrt{\pi}}{12} (k\delta)^2 I_1 - (k\delta/3) I_2 + \frac{\sqrt{\pi}}{8} I_3 \right], \quad (8)$$

where

$$D = \left[\frac{\sqrt{\pi}}{6} (k\delta)^2 - 4k\delta/3 + 2\sqrt{\pi} \right],$$

$$I_1 = \int_{y_s}^{y_m} (I/I_0)(y_s/y)^{1/2} (dy/y),$$

$$I_2 = \int_{y_s}^{y_m} (I/I_0)(y_s/y)^{1/2} \ln(y/y_s) (dy/y),$$

$$I_3 = \int_{y_s}^{y_m} (I/I_0)(y_s/y)^{1/2} \{\ln(y/y_s)\}^2 (dy/y),$$

$$y_s = \gamma^{1/3} F_s^{-2/3} (E_g - \hbar\omega),$$

$$y_m = \gamma^{1/3} k^{-2/3} (E_g - \hbar\omega)^{1/3},$$

and

$$I = I_0 \text{ at } \hbar\omega = E_g.$$

2.2 Mechanical stress

Thin films are generally characterized by the presence of a large number of defects and the existence of high stress. The polycrystalline films are described by the

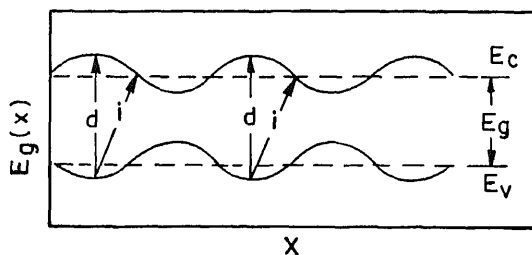


Figure 2. Qualitative picture of deformed valence and conduction band edges of polycrystalline semiconductors.

presence of alternate grains (crystallites) and grain-boundary (amorphous) regions. This would amount to the presence of large stresses in the grain-boundary regions (Szczyrbowski 1979; Klyava 1985; Gavrilenko 1987). Thus, besides the grain-boundary electric field effect, the mechanical stress due to lattice dilation at the grain-boundary regions which may include permanent lattice disorder (in the grain and grain-boundary regions) and thermal lattice disorder also influence the electronic structure and hence the below-band-edge optical absorption processes as a whole.

The influence of mechanical stress in the grain boundary region of polycrystalline films has been associated with electrostatic fluctuations of the band edge (figure 2) by several authors (Szczyrbowski 1979; Klyava 1985; Gavrilenko 1987). The basic idea of the above model is the existence of a finite probability of transitions between states lying at different sites in the polycrystalline sample. This will control the specific shape of the absorption tail in the below-band-edge absorption region. Besides these indirect transitions, allowed direct transitions may also occur simultaneously in these polycrystalline films. But the latter will predominate only in the photon energy region $\hbar\omega > \bar{E}_g$. $\bar{E}_g$ is the average value of the fluctuating E_g in the grain and grain-boundary regions. So we will not consider the contribution from the latter on the tail of the optical absorption.

In order to calculate the absorption due to mechanical stress, we consider first the variation of E_g in various sites of the specimen by the following distribution function (Szczyrbowski 1979, 1981):

$$D(E_g) \sim \exp \left[\frac{-(E_g - \bar{E}_g)^2}{2\sigma^2} \right], \quad (9)$$

where $\sigma^2 = E_g^2 \bar{\Delta}^2$, $\bar{\Delta}^2 \sim a/4L_c$, L_c being the characteristic length over which E_g is assumed to be constant and a the average lattice constant. For polycrystalline material, the characteristic length is set equal to the Debye screening length (λ_d) in this case. Physically, the parameter $\bar{\Delta}$ is a relative local and thermal fluctuating dilation constant and depends on the grain size and shape of the polycrystalline film and its lattice temperature.

Now, the general form of the absorption coefficient $\alpha^M(\hbar\omega)$ due to mechanical stress may be expressed as

$$\alpha^M(\hbar\omega) \sim \int_{\hbar\omega}^{\alpha} P(E) D(E_g) dE_g, \quad (10)$$

where $D(E_g)dE_g$ is proportional to the number of microcrystallites per unit volume and $P(E)$ is the probability of indirect transitions within the region of the sample in which the energy gaps are between E_g and $E_g + dE_g$.

Assuming the form of $P(E)$ as given by Szczyrbowski (1979, 1981):

$$P(E) = P_0 \exp[(\hbar\omega - E_g)/E'], \quad (11)$$

where $E' = 3\sqrt{[(\hbar^2 k^2 \sigma^2)/6m_e]}$ and substituting (9) in (10), the final form of $\alpha^M(\hbar\omega)$ after simplification becomes

$$\alpha^M(\hbar\omega) = \alpha_0^M \exp[(\hbar\omega - E_0)/E'] \Phi(\hbar\omega), \quad (12)$$

where α_0^M is the value of $\alpha^M(\hbar\omega)$ at E_g , $E_0 = E_g - \sigma^2/2E'$, and $\Phi(\hbar\omega)$ is a slowly varying function written as

$$\Phi(\hbar\omega) = E_g^{-1} \int_{\hbar\omega}^{\infty} \exp[-(\sigma^2/2E'^2)] dE_g. \quad (13)$$

In the photon energy region $\hbar\omega \leq E_g$ which is of special interest to us here, the above function $\Phi(\hbar\omega)$ is almost constant and its explicit form may be given by

$$\Phi(\hbar\omega) = \left(\frac{\hbar^2 k^2}{6m_e}\right) E_g^{-1} \exp[-(\bar{\Delta}^2)^{1/3}/2] \int_{x_{\min}}^{x_{\max}} \exp(-x^{2/3}) dx, \quad (14)$$

with

$$x_{\min} = 6m_e \hbar\omega / \hbar^2 k^2 \text{ and } x_{\max} = 6m_e E_g / \hbar^2 k^2.$$

In a real situation, the inclusion of finite grain size distribution as given by (6) will modify the expression of $\alpha^M(\hbar\omega)$, i.e. (12), as

$$\alpha^M(\hbar\omega) = \alpha_0^M \exp[(\hbar\omega - E_g)/C_0] \theta(R) \Phi(R, \hbar\omega), \quad (15)$$

where $\theta(R) \sim \int_{R_{\min}}^{R_{\max}} \exp(-X_0) R^2 dR$, with $C_0 = [(\hbar^2 k^2 E_g^2)/48m_e]^{1/3}$, $\Phi(R, \hbar\omega) \sim$

$\Phi(\hbar\omega)$, and $X_0 = (R/\delta)^2 - (R/a)^{1/3} - \frac{E_g^2}{16C_0(E_g - \hbar\omega)}(a/R)^{1/3}$. The inclusion of the grain distribution has a negligible influence on $\alpha^M(\hbar\omega)$.

By using (8) and (15), one can get the total below-sub-band-edge absorption $\alpha = (\alpha^E + \alpha^M)$ and hence (α/α_0) due to grain-boundary effects. The best fit of this simple theoretical model to the experimental plots will provide meaningful information on the grain-boundary potentials, density of trap states, carrier concentration, etc of polycrystalline semiconductor films.

The above exercise becomes meaningful when one can obtain the absorption data quite accurately. The films being polycrystalline, surface roughness will play a dominant role in determining transmittance and reflectance in the films. Scattered transmittance (T_{scatter}) and diffuse reflectance (R_{diff}) are sure to make a significant contribution (Bennett and Bennett 1967; Tuttle *et al* 1989; Bhattacharyya *et al* 1992b) in the evaluation of the absorption coefficient (α). In recent communications (Bhattacharyya *et al* 1992a,b), we could show that, by measuring reflectances of a film from the film side (R) and the substrate side (R_1), one can calculate the absorption

data with sufficient accuracy so as to incorporate (Bhattacharyya *et al* 1992a) the behaviour of the absorption versus wavelength as demanded by the theory. We could also show (Bhattacharyya *et al* 1992b) that by measuring R and R_{diff} , one can obtain the grain size and grain distribution quite accurately. This will mean that just by measuring the reflectances R , R_1 and R_{diff} as depicted in the previous communications (Bhattacharyya *et al* 1992a,b) one can measure the absorption coefficient and the grain size quite accurately to use the expressions (8) and (15) for deriving meaningful information on the grain-boundary potential, density of trap states and carrier concentration of a high-resistivity semiconductor film.

3. Experimental observations

Figure 3 shows the variation of α/α_0 versus $(E_g - \hbar\omega)$ for ZnTe film deposited onto glass substrate at a temperature of 553 K by the hot wall evaporation technique (Maiti *et al* 1994). The individual contributions from the electric field effects (8) and the mechanical effects (15) are shown in figure 3 along with the total theoretical α/α_0 values. For theoretical simulation of the below-band-edge absorption curve, we used the values of different parameters as follows:

$m_e = 0.10 m_0$; $m_h = 0.6 m_0$; $\Delta_0 = 0.91$ eV; $a = 6.085$ Å (obtained from XRD traces) and $\bar{R} = 0.138$ nm (derived from reflectance measurements, Bhattacharyya *et al* 1992b). The values of optical constants, $E_g = 2.275$ eV, $n = 2.7$ and $\alpha = 9512 \text{ cm}^{-1}$ at photon energy $h\nu = E_g$, used here were reported in Maiti *et al* (1994).

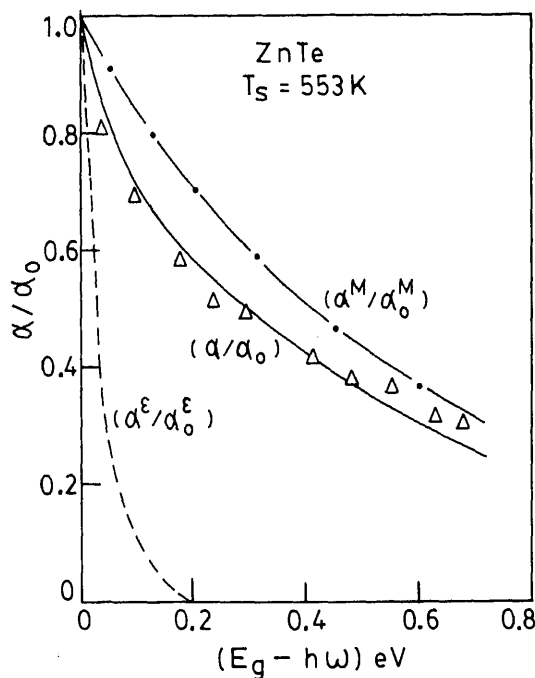


Figure 3. α/α_0 vs $(E_g - \hbar\omega)$ plots for ZnTe films: Δ , experimental points; ---, α^E/α_0^E ; - · - · -, α^M/α_0^M ; —, total α/α_0 ($\alpha = \alpha^E + \alpha^M$).

In the course of the best theoretical fitting procedure, we first chose some guess values of F_s and k for generating the contribution from electric field while a guess value for λ_d was used for evaluating the contribution of the effect due to mechanical stress. Then by using (8) and (15) and by adopting an iterative technique, we could easily obtain the best simulated value for the fit of the experimental data.

It can be observed that the contributions arising from the existence of mechanical stresses in polycrystalline semiconductor films are quite significant in describing the shape of the absorption curve beyond the absorption edge. The fit of the experimental data (α/α_0) with the theoretical values of (α/α_0) evaluated by considering the contributions from both the grain-boundary effect and mechanical stress is remarkable. The density of trap states (Q_t) and the barrier height (E_b) computed from the above fit for ZnTe films were found to be $5.013 \times 10^{12} \text{ cm}^{-2}$ and 0.205 eV respectively, which compare well with those obtained earlier (Maiti *et al* 1994).

4. Conclusions

The effect of grain boundaries on the optical absorption below the band edge in polycrystalline semiconductor films has been considered. It was observed that the band tailing could be effectively explained by considering the effects of inherent electric field and mechanical stress simultaneously present at the grain boundaries. A realistic approach to the above problem was conceived by incorporating the actual surface roughness and grain distribution present in the films. The above theory was successfully applied to generate information on the barrier height and density of trap states present at the grain boundaries of ZnTe films.

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Magnetoelectric interaction phenomena in materials

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Abstract. Following the phenomenological approach of Landau and Lifshitz the existence of linear magnetoelectric effect in antiferromagnetic Cr_2O_3 was predicted by Dzyaloshinskii which was later experimentally confirmed by Astrov and Folen *et al.* Magnetoelectric phenomenon has been observed in several single-phase materials in which simultaneous electric and magnetic ordering coexists and in two-phase composites in which the participating phases are the ferroelectric and magnetic. The author's group has recently undertaken a systematic study of the preparation, characterization and detection of the $(\text{ME})_H$ output in a few single-phase materials and two-phase composites. This article describes the magnetoelectric phenomenon in general and recent work carried out in the author's group.

Keywords. Magnetoelectric; ferroelectric; anti-ferromagnetic; composite.

1. Introduction

The consideration and analysis of interactions between various subsystems in a crystal forms an important branch of contemporary condensed matter physics. In a variety of materials several new effects have been discovered on the basis of interactions between subsystems in a crystal. In some insulating materials, an external magnetic field can induce electric polarization and an external electric field induces changes in magnetization. Such a phenomenon is called the magnetoelectric (ME) effect. The ME effect observed in some insulating materials offers a challenge to both experimental and theoretical scientists, since the materials showing the ME effect belong to an entirely new class.

In the last century Curie (1894) presumed the existence of ME effect in some crystals. The statement of Curie that the symmetry conditions show us that it would be possible for asymmetric molecular body to polarise directionally when one places it in a magnetic field is historic. On the basis of the symmetry considerations Landau and Lifshitz (1957) came to the conclusion that the ME effect can exist, in principle, in a magnetically ordered crystal. The starting point for research on an actual crystal was marked by the theoretical prediction of occurrence of ME effect by Dzyaloshinskii (1959) in the antiferromagnetic Cr_2O_3 . Shortly after this, Astrov (1960, 1961) and Folen *et al* (1961) reported the experimental observation of $(\text{ME})_E$ and $(\text{ME})_H$ in Cr_2O_3 .

As mentioned earlier, the ME phenomenon is due to magnetic and electric interaction in certain crystals. From simple thermodynamic principles this could be expressed in power series in terms of external magnetic field dH and the electric field dE as

$$F = F_0 - P_0 \cdot \bar{E} - M_0 \cdot \bar{H} - 1/2 \chi_{ij}(E) \cdot \bar{E}_i \bar{E}_j - 1/2 \chi_{ij}(H) \bar{H}_i \bar{H}_j - \alpha_{ij} \bar{E}_i \bar{H}_j \dots, \quad (1)$$

where F is the total Gibbs free energy and F_0 the free energy independent of E and H , $\chi(E)$ and $\chi(H)$ are electric and magnetic susceptibility tensors, and α_{ij} is the magnetoelectric tensor (Schmid 1965; Rado 1975).

From (1), differentiating F with H gives magnetic moment and with E gives electric polarization:

$$M_i = (-\partial F/\partial H) = M_0 + \chi_{ij}\bar{H}_j + \alpha_{ij}\bar{E}_j,$$

$$P_i = (-\partial F/\partial E) = P_0 + \chi_{ij}\bar{E}_j + \alpha_{ij}\bar{H}_j,$$

where the α_{ij} s are the respective magnetoelectric tensors corresponding to $(ME)_H$ and $(ME)_E$. The number of components of this tensor depends upon the symmetry of the magnetic point group. In (1) the terms which occur after the α s, on further expansion of the series, would lead to higher-order magnetoelectric coefficients, viz. β_{ijk} etc.

During the last 35 years after the discovery, linear ME effect has been observed in many compounds, including Fe_3O_4 and YIG. Higher-order effects were also discovered experimentally. The ME effect is not so large in magnitude and, as mentioned earlier, the effect is restricted to insulators. From a thermodynamic point of view, the $(ME)_E$ and $(ME)_H$ effects are converse to each other and if one exists the other must also exist. However, from an experimental standpoint, the situation is not so simple.

Stimulated by the announcement by Smolenskii and Joffe (1958) of the synthesis of $Pb(Fe_{1/2}Nb_{1/2})O_3$, the first antiferromagnetic ferroelectric perovskite, and in an attempt to find interesting ME properties, many workers tried to find antiferromagnetically and ferromagnetically ordered ferroelectrics and antiferroelectrics. Due to these efforts, a large variety of magnetoelectrically interesting compounds have been discovered, a few of which are remarkable because of interactions between spontaneous polarization and spontaneous magnetization. Special mention is to be made of the work of Schmid and his group on a number of boracites belonging to a large family of crystals with the general formula $Me_3B_7O_{13}X$, where Me stands for a bivalent metal ion such as Mg, Cr, Mn, Fe, Co, Ni, Cu or Zn, and X for a monovalent anion like F, Cl, Br or I. Ismailzade *et al* (1980) studied a number of solid solutions based on $BiFeO_3$ and $BaTiO_3$, and $BiFeO_3$ -PZT for their ME effects.

The ME effect has also been reported in single-phase materials having the perovskite structure, RE manganates, $BaMF_4$ ($M = Mn, Fe, Co, Ni$), inverted spinels, pseudosilmenites, Cr_2BeO_4 , etc. (Smolenskii and Chupis 1984). The ME effect can be observed in either a single-phase material or a composite. Some single-phase materials, exhibiting simultaneous combination properties as listed below, are suitable candidates for observation of the ME effect. The combination properties are: ferroelectricity-ferromagnetism, ferroelectricity-ferrimagnetism, ferroelectricity-antiferromagnetism, antiferroelectricity-ferrimagnetism, antiferroelectricity-antiferromagnetism. The amount of the output signal depends on the strength of interaction between the two subsystems. Most single-phase materials studied so far have shown ME effects at low temperatures.

There is also a second approach to realize the ME conversion through composite materials. Following the concept of product properties of composites, introduced by Van Suchtelen (1972), suitable combination of piezomagnetic (phase I) and piezoelectric (phase II) phases can also give rise to the ME effect. The constituent submaterials I

. The transfer of the Y parameter from submaterial I to submaterial II can be brought about by the coupling mechanism

$$(X/Y) \cdot (Y/Z) = X/Z,$$

$$(H/P) \cdot (P/E) = H/E \rightarrow \text{ME effect},$$

where H is the applied magnetic field, P the polarization and E the electric field. In a composite consisting of piezomagnetic and piezoelectric phases, the applied magnetic field would induce a strain in the magnetostrictive phase, which, in turn, through mechanical coupling, causes a stress in the piezoelectric phase by which an electric field is generated.

O'Dell (1970), Skinner (1970), Freeman and Schmid (1975), Smolenskii and Chupis (1984), Tolendano *et al* (1985) and Siratori *et al* (1992) may be consulted for reviews on ME interaction phenomena in crystals.

The author's group has recently undertaken a systematic study of the preparation, characterization and detection of $(ME)_H$ output in a few single-phase and two-phase systems.

Experimental

The materials were prepared by solid-state double sintering method. The formation of phases was identified by XRD and optical microscopy. The electrical conductivity was determined by a two-probe DC technique and the dielectric data were obtained using a HP 4192 impedance analyser. The essential requirement of any material to exhibit ME output is that it should possess a high value of resistivity. The materials have to be poled electrically and magnetically before the ME measurements are made. A suitable strategy of poling has to be employed for each material. While the experimental set-up for the characterization of most of the other physical properties is well known, we restrict ourselves only to give a few details regarding the detection of the DC ME signal. The ME signal can be measured either in static fields or in dynamic fields. We have made only static measurements.

1 Experimental set-up to measure DC $(ME)_H$

The experimental set-up to measure ME signal is shown in figure 1. The sample holder is made of Perspex having dimensions indicated in figure 2. Two copper electrodes were brazed to the electrical leads and were kept on either side of the poled sample. The sample is kept between the two Perspex blocks. The whole sample holder assembly was kept between the pole pieces of a DC electromagnet. All stray pick-ups have been avoided by proper grounding of the experimental set-up. The two ends from the sample were connected to a 610C electrometer through a shielded cable. The measurement of output voltage is made after stabilization on the application of the magnetic field. The steady value of the voltage was noted after waiting for 10 min. This long duration was required because of the high response time of the

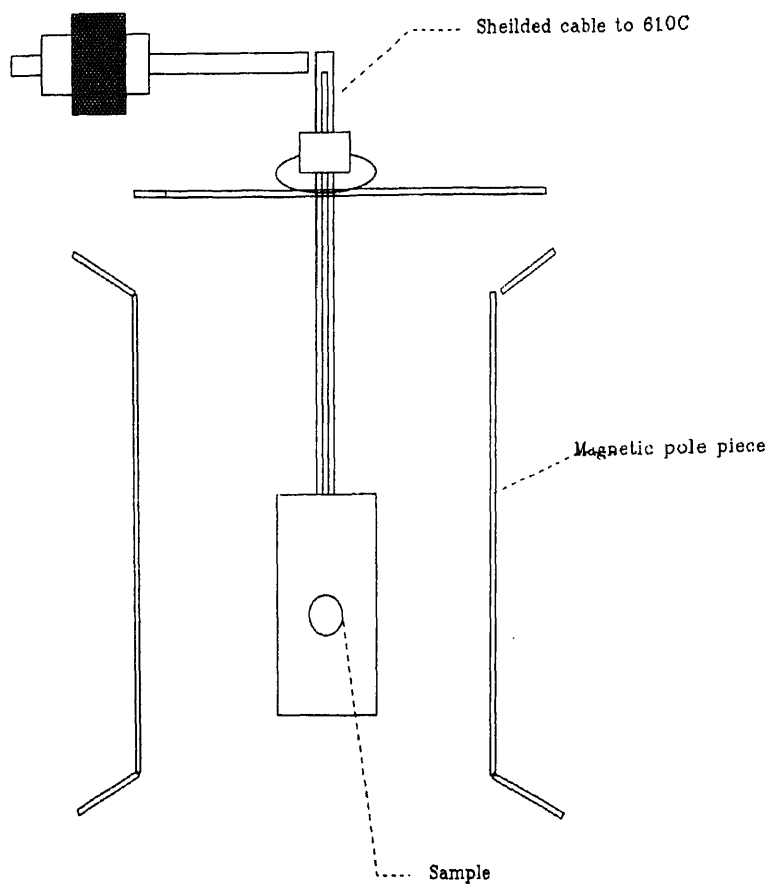


Figure 1. Set-up for measurement of MEC.

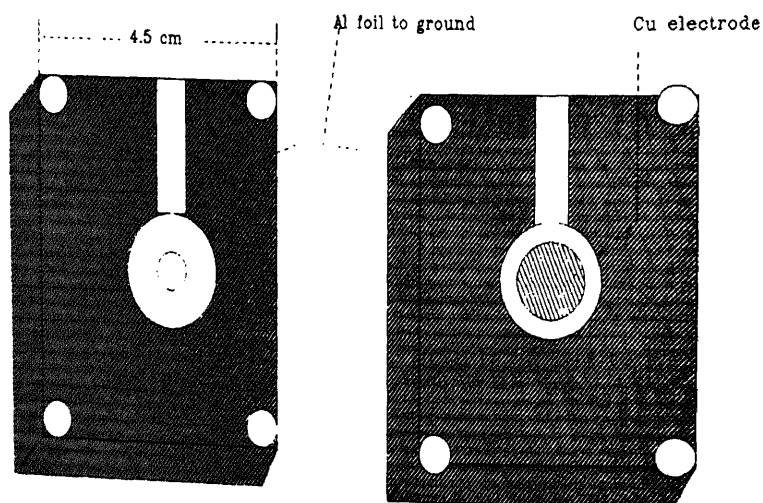


Figure 2. Sample holder for MEC measurements.

analog meter. The output voltage developed across the sample was measured as a function of increasing and decreasing DC magnetic fields.

2. Single-phase materials

There is a large family of oxides with general formula $\text{Bi}_2\text{M}_{n-1}\text{R}_n\text{O}_{3n+3}$, where $n = 1, 2, 3, 4, 5, \dots$ (Aurivillius 1949), exhibiting interesting physical property variations and phase transitions. The cubo-octahedral M site accepts Bi, Ba, K, Ca, Na, Pb and several rare-earth ions, while the smaller Ti, Nb, Ta, Fe, W, Mo and Cr ions go into the octahedral R sites. There are more than 50 compounds in the group. The recently discovered bismuth-based superconductors also have an origin in the Aurivillius (1949) phases.

Among the different compounds that form from the general formula mentioned, those with $\text{M} = \text{Bi}$ and $\text{R} = \text{Fe/Ti}$ were found to be interesting with different values of n because of dielectric anomalies at high temperatures and also possible ME interaction. Further BiFeO_3 is an interesting material because of its antiferromagnetic-ferroelectric nature and also because of the controversy about its ME output. Schmid (private communication) has reported it to be a second-order magnetoelectric material in which the first-order ME coefficient would not exist because of magnetic symmetry. But Ismailzade *et al* (1980) reported the presence of linear ME coefficient in a polycrystalline BiFeO_3 . Further, bismuth titanate is considered as a second cousin of BaTiO_3 having high resistivity. The combination of these two materials would yield interesting ME materials because of the reported layer structure. We have chosen the three combinations of these two, by varying the value of n in the generic formula mentioned earlier. The same formula now could be written specifically for these compounds as $\text{Bi}_4\text{Bi}_{m-3}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$. The compounds with $m = 4, 5$ and 8 could be formed as $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$, $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ and $\text{Bi}_9\text{Fe}_5\text{Ti}_3\text{O}_{27}$ respectively, whereas compounds with $m = 6$ and 7 cannot be formed. These three compounds have been reported to show simultaneous existence of ferroelectric and magnetic nature up to very high temperatures. This is the precondition for the material to be magnetoelectric. The preparation and characterization of $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ will be discussed in some detail and for the others only the final results will be presented (Singh *et al* 1994a).

3.1 $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ and related materials

The compound was formed by solid-state reaction method by taking Bi_2O_3 , Fe_2O_3 and TiO_2 in molar proportions. They were presintered at 850°C for 2 h and later anneal-sintered at 1050°C for 2 h. The XRD pattern obtained for these samples was compared with that of Ismailzade *et al* (1967). The average density measured was 8.87 g/cm^3 . X-ray density was found to be 8.03 g/cm^3 indicating that the pellets formed had negligible porosity. The samples were essentially poled at 150°C in an electric field of 10 kV/cm . The dielectric measurements were performed using a HP impedance analyser in the temperature range RT to 850°C at a fixed frequency of 10 kHz in order to avoid the effect of space charge polarization, if any. A hump around 750°C was observed, but no sharp transition in the dielectric measurement was observable.

The magnetoelectric measurements were performed on this material by selecting

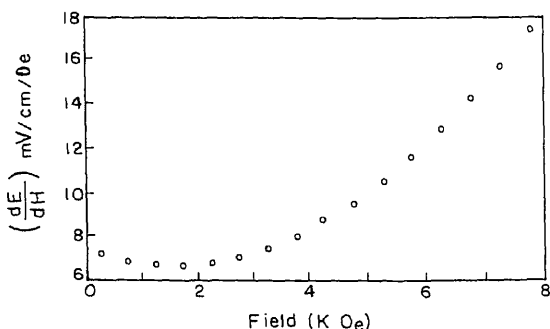


Figure 3. dE/dH vs field of $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$.

a disk of 1 mm thickness. The sample was electrically poled as mentioned above and was also poled magnetically in a field of 9 kOe. The magnetoelectric signal was obtained by measuring the voltage developed across the sample as a function of applied DC magnetic field up to 8 kOe.

The variation of dE/dH vs H is shown in figure 3. The maximum value of dE/dH observed was 17 mV/Oe/cm at 8 kOe. It was also observed that when the magnetic field was reduced, the electric polarization did not decrease indicating thereby that the electric charges have been locked at the grain boundaries. Heating of such a sample brought the polarization to zero indicating that this material could be an example of an electret. The measurement of ME coefficient in this sample was made possible due to its high value of resistivity, viz. 5.8×10^{11} ohm-cm at room temperature. The polarization induced could be due to the displacement of Fe ions, thereby changing the ionic polarizability or creating quasi-permanent dipoles. The complete data for this sample are given in table 1 (Singh *et al* 1994a).

Following a similar preparation technique, $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ and $\text{Bi}_9\text{Fe}_5\text{Ti}_3\text{O}_{27}$ were also prepared. These two compounds also showed high value of resistivity. The ME coefficient in $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ was found to be 3.2 mV/cm/Oe at 4 kOe (Singh *et al* 1994b) which is less than that of $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$. The ME measurements in $\text{Bi}_9\text{Fe}_5\text{Ti}_3\text{O}_{27}$ (Singh, unpublished) did not yield any result indicating thereby that ME interactions in these samples are very weak. Therefore from table 1 one could observe that, as the Fe content increased, the ME interaction decreased, thereby affecting the ME coefficient.

We have reinvestigated BiFeO_3 which also has an impurity phase of $\text{Bi}_2\text{Fe}_4\text{O}_9$. The resistivity of our sample was however very large (10^{12} ohm-cm) compared to that reported by Schmid (1994). After usual electrical and magnetic poling, DC ME measurements were performed. The ME coefficient obtained in the sample was of first order as reported by Ismailzade's (1967) group. The ME coefficient observed was however lower than that of four-layer and five-layer compounds but measurable, and is equal to 64 $\mu\text{V/cm/Oe}$ at 9.5 kOe. Further studies on BiFeO_3 are in progress.

4. Two-phase materials

Boomgaard *et al* (1974) prepared composites of piezoelectric and piezomagnetic phases and detected the magnetoelectric output. The piezomagnetic phase chosen was

Table 1. Data for single-phase Bi-based materials.

	BiFeO ₃	Bi ₄ Ti ₃ O ₁₂	Bi ₅ FeTi ₃ O ₁₅	Bi ₆ Fe ₂ Ti ₃ O ₁₈	Bi ₉ Fe ₅ Ti ₃ O ₂₇
Structure	Rhombohedral	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
ϵ (10 kHz)	38	90	97	98	94
T_c (°C)	850	675	No sharp peak	795	740
Resistivity (ohm-cm)	10 ¹²	10 ¹²	10 ¹²	10 ⁹	10 ¹⁰
χ_m (DC)	1.5 × 10 ⁻⁷	—	1.85 × 10 ⁻⁷	2.89 × 10 ⁻⁷	3.42 × 10 ⁻⁷
emu/mol					
Magnetostriction	Not detectable	—	Not detectable	Not detectable	Not detectable
B-H	Not traceable	—	Not traceable	Not traceable	Not traceable
Nature	AFM/FE	FE	AFM/FE	AFM/FE	AFM/FE
dE/dH max mV/cm/Oe	0.064	—	17	3.2	Not detected
	*		**	***	
Remarks (No. of layers)	—	3	4	5	8

*at 9.5 kOe; **at 8 kOe; ***at 4 kOe.

$\text{Ni}(\text{Co}, \text{Mn})\text{Fe}_2\text{O}_4$ and the piezoelectric phase was BaTiO_3 . They observed the higher ME conversion of 130 mV/cm/Oe in unidirectionally cooled composite of 60% $\text{Ni}(\text{Co}, \text{Mn})\text{Fe}_2\text{O}_3$ –40% BaTiO_3 than in the same composite prepared by double sintering method. They have also studied the dependence of dE/dH on various process parameters, compositions, and particle sizes of the composites. Experimentally it is easier to prepare composites by double-sintering process than the unidirectional cooling. The existence of a eutectic point or a eutectoid phase is a prerequisite for unidirectional cooling. The following are the advantages of solid-state sintering: (a) free choice of mole ratio of constituent phases and sintering temperatures, (b) independent choice of grain size of each phase.

To realize higher output of ME conversion in composite materials the following guidelines are to be kept in mind (Boomgaard *et al* 1977).

- (i) The two phases must be in equilibrium.
- (ii) Mechanical contact between grains must be perfect.
- (iii) The value of magnetostriction coefficient of piezomagnetic phase must be high.
- (iv) The value of piezoelectric coefficient of the piezoelectric phase must be high.
- (v) The accumulated charges must not leak through the piezomagnetic phase. Hence this phase should have resistivity $> 10^8$ ohm-cm.
- (vi) $T_c \gg R_f$ to facilitate poling and the relaxation time for charge compensation is to be longer.
- (vii) Proper poling strategy is to be adopted for the material to show higher ME conversion.

We have studied composites of CoFe_2O_4 – BaTiO_3 (Hanumaiah *et al* 1994), NiFe_2O_4 – BaTiO_3 , LiFe_5O_8 – BaTiO_3 (Suryanarayana *et al* 1994), CoFe_2O_4 – $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The CoFe_2O_4 – BaTiO_3 composites have been prepared by solid-state double-sintering route. The samples were characterized by XRD. The sign of ME conversion in the samples depended on the polarization direction of the ferroelectric phase. Therefore the electrical poling was done for all samples at 150°C which is 30°C above the ferroelectric transition temperature of BaTiO_3 . At room temperature the applied electric field was 7.5 kV/cm. The field started decreasing at around 90°C and was about 3–5 kV/cm at 150°C depending on the composition. The samples were kept at this temperature for 30 min and were cooled to room temperature in the presence of the external field. Later the samples were subjected to magnetic poling in a DC magnetic field.

The dielectric permittivity ϵ_r of all the composites of cobalt ferrite–barium titanate have been measured in the temperature range room temperature to 130°C, for which silver-coated pellets were used. Using a HP 4192A impedance analyser, the dielectric measurements were carried out at 10 kHz. In these composites, with increasing concentration of BaTiO_3 the T_c was found to increase from 115°C to 120°C. The ME coefficient (dE/dH) of the composites, which is the product of piezomagnetic deformation and the piezoelectric generation, largely depends on the electrical resistivity of the sample and the mechanical coupling between the two phases.

We have measured ME conversion for three compositions of CoFe_2O_4 – BaTiO_3 as a function of DC magnetic field. The ME conversion factor for different magnetic fields from 0.1 kOe to 2 kOe was determined by measuring the voltage across the sample with a 610C Keithley electrometer. Figure 4 shows the typical dependence of magnetoelectric conversion on magnetic field for three composites studied. The

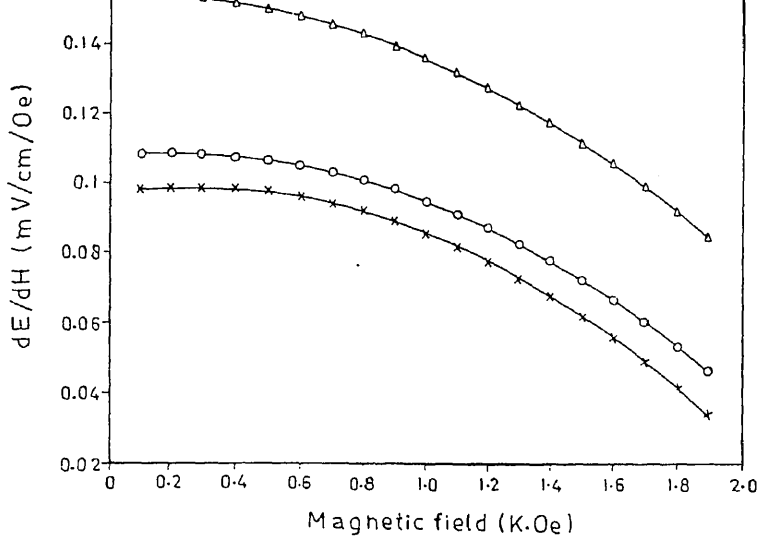


Figure 4. dE/dH vs field of cobalt ferrite-barium titanate composite. (x, 60% CoFe_2O_4 -40% BaTiO_3 ; o, 50% CoFe_2O_4 -50% BaTiO_3 ; Δ, 40% CoFe_2O_4 -60% BaTiO_3).

maximum value of dE/dH observed in a composition containing 60 mole% of BaTiO_3 is $160 \mu\text{V/cm/Oe}$. From figure 4 it is seen that the value of dE/dH decreases with increasing magnetic field beyond 600 Oe for all three composites. As already mentioned, the magnetoelectric conversion is the result of piezomagnetic strain in spinel phase which creates piezoelectric charge in the ferroelectric phase and hence the latter would depend upon the variation of piezomagnetic coefficient with intensity of magnetic field. In the spinels, the magnetostrictive coefficient reaches a saturation at a certain value of magnetic field. In the case of CoFe_2O_4 the magnetostriction as well as the intensity of the magnetic field reaches saturation around 600 Oe (Cullity 1972). Therefore, beyond this field, the magnetostriction and the strain thus produced would also produce a constant electric field in the piezoelectric phase, hence making the dE/dH decrease with increasing magnetic field. Our figures for CoFe_2O_4 - BaTiO_3 composites prepared by solid-state route are much lower than those of Boomgaard *et al* (1974). The lower values obtained in this work may be attributed to the spinel phase having resistivity less by about 4-5 orders of magnitude than the piezoelectric phase. Presumably the ferrite phase offers a leakage path for the charges developed across the piezoelectric phase.

4.1 LiFe_5O_8 - BaTiO_3

Velleaud *et al* (1982) reported that LiFe_5O_8 single crystal shows magnetoelectric conversion at 6 K. They observed second-order magnetoelectric effect along (001) direction at 6 K. We have prepared composites of LiFe_5O_8 - BaTiO_3 to look for possible ME conversion at room temperature. The composites have been prepared by solid-state double-sintering method in which there was no detectable ME signal.

However, in a second batch of preparation, LiFe_5O_8 was prepared by sol-gel method and composites of $\text{LiFe}_5\text{O}_8\text{-BaTiO}_3$ were made. The composites prepared from the sol-gel LiFe_5O_8 exhibited a high resistivity and comparatively high dielectric constant. The magnetoelectric conversion also could be detected. In a recent communication from our laboratory the details of this study have been reported (Suryanarayana *et al* 1992). In figure 5 we present the data for dE/dH . In table 2 we summarize the results.

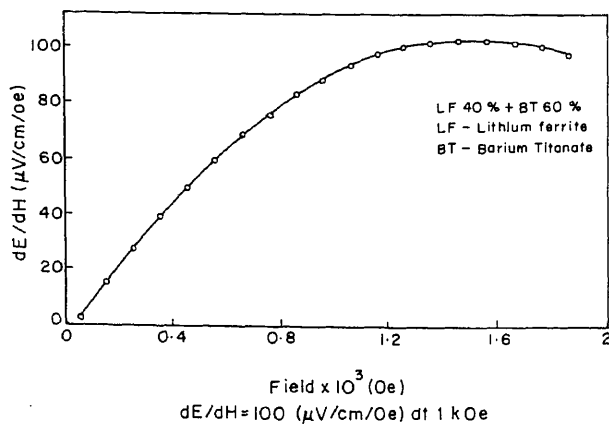


Figure 5. dE/dH vs field of lithium ferrite-barium titanate composite.

Table 2. Data for composites

Composition	ϵ	Resistivity (ohm-cm)	T_c (°C)	ME
Solid-state route				
CF + BT				
60 40	209	10^8	115	$100 \mu\text{V/cm/Oe}$
50 50	98	10^8	117	$109 \mu\text{V/cm/Oe}$
40 60	144	10^9	120	$160 \mu\text{V/cm/Oe}$
LF + BT				
60 40	540	10^8	50	No signal
50 50	815	10^9	50	No signal
40 60	890	10^{10}	50	No signal
(Sol gel)				
60 40	80	10^{10}	92	No signal
40 60	102	10^9	102	$100 \mu\text{V/cm/Oe}$
NF + BT				
60 40	620	10^7	107	$300 \mu\text{V/cm/Oe}$
40 60	718	10^8	99	$450 \mu\text{V/cm/Oe}$
CF + BIT(SS)				
50 50	90	10^9	675	$120 \mu\text{V/cm/Oe}$

NF, Nickel ferrite; BT, barium titanate; LF, lithium ferrite; CF, cobalt ferrite; BIT, bismuth titanate.

Wood and Austin (1974) indicated possible applications of magnetoelectric crystals as well as the characteristics of over 15 devices whose operation range varies from audio to optical frequency, including modulators, switches, phase invertors, rectifiers, etc. Materials showing ME conversion can also be used as thin-film wave guides in integral optics and fibre communication technology.

The research on ME effect seems to be less popular among physicists in recent times compared to the works of the first generation. Though the magnitude of the effect in terms of the output is small, it gives a unique technique for the study of the properties of materials both in single-phase and composite form. There are many materials exhibiting simultaneous electric polarization and magnetic ordering which may be good candidates for the study of ME interactions. Here is an area of research for generations of materials scientists to involve themselves in materials engineering with a view to achieve higher yield of ME coefficients to explore the possibility to identify suitable materials for yet unexplored applications. Our group is presently engaged in such activity.

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Non-resonant RF and microwave response: A novel technique for the characterization of superconducting materials

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Abstract. When examined using continuous wave electron paramagnetic resonance and nuclear magnetic resonance spectrometers, the high T_c superconductors give rise to intense, low field, 'non-resonant' absorption signals in the superconducting state. This phenomenon can be used as a highly sensitive, contactless technique for the detection and characterization of superconductivity even in samples containing only minute amounts of the superconducting phase. Further, it can also be applied to the determination of material parameters of interest such as J_c and H_{c2} in addition to being a powerful way of distinguishing between weak-link superconductivity and bulk superconductivity. The details of these aspects are discussed.

Keywords. Non-resonant microwave absorption; high-temperature superconductors; weak-links; fluxon motion.

1. Introduction

The study of electrodynamic properties of superconductors subjected to magnetic fields is important from both the fundamental and technical points of view. Not only can it provide a test for any plausible microscopic theory of superconductivity but it can also yield information on the material parameters important for many of the technological applications. After the advent of the high- T_c superconductors (Bednorz and Muller 1986; Chu *et al* 1987), a new, highly sensitive method of studying the response of superconductors to electromagnetic radiation has come into vogue. It is based on the observation (Bhat *et al* 1987a, b) that when examined using conventional continuous wave (CW) electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) spectrometers, the new superconductors exhibit at low magnetic fields, in the superconducting state, intense signals even with minuscule amounts of the samples. The high sensitivity of the technique arises because of the magnetic field modulation and lock-in detection commonly used in the CW EPR and NMR spectrometers. In the absence of hysteresis, the technique yields the field derivative, dP/dH , of the power absorbed by the sample. The properties of these derivative signals are very sensitively dependent on temperature, applied magnetic field, and quite often on the nature and quality of the samples. First observed in ceramic samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Y}_{0.75}\text{Lu}_{0.25}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ by us (Bhat *et al* 1987a, b) this phenomenon is found to occur in different forms of these materials like single crystals and thin films as well as the ceramics. Keeping up with the pace of the activity in other areas of superconductivity research, over the last seven years a large number (> 150) of papers have appeared on this subject (for an early review see Blazey 1990). As a consequence, many of the earlier uncertainties regarding the nature of the phenomenon have been clarified. In this article, we plan to indicate the applications of the technique to two specific cases of importance to materials research, namely the measurement of the critical current density J_c and the characterization of the samples for the

presence of weak links and the determination of the nature of the weak links that are present.

2. Early experimental results

The first observation of the non-resonant microwave absorption phenomenon in the high- T_c superconductors was actually made during an attempt to study the EPR of Cu^{2+} in ceramic samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The attempt was motivated by the fact that EPR is known, from the earlier studies of conventional superconductors (Baberschke 1976), to be one of the useful techniques to study superconductivity. In our initial experiments (Bhat *et al* 1987a) it was observed that a signal with an anisotropic g parameter of ~ 2 and attributable to Cu^{2+} ion was present in the normal state of the compound. The signal disappeared below T_c accompanied by an increase in the spectrometer noise. [Now it is well established that a pure single-phase superconducting material does not give rise to any Cu^{2+} EPR signal either in the normal state or in the superconducting state. Some of the possible reasons for this 'EPR silence' in these materials are discussed by Mehran and Anderson (1989). Very interestingly, however, an intense signal (figure 1) appeared just below T_c centred around zero magnetic field and continued to evolve in the superconducting state. The following properties of this signal were noted:

- (i) The signal was very narrow (~ 10 Oe) and much stronger than the $g \sim 2$ signal and disappeared on warming the sample to $T > T_c$.
- (ii) During warming, while the intensity of the signal went on decreasing, a few degrees below T_c the phase of the signal reversed.
- (iii) For low modulation amplitudes, the signals for the forward and the backward magnetic field sweeps showed pronounced hysteresis, in as much as the phases of signals for the two opposite scans were completely opposite.

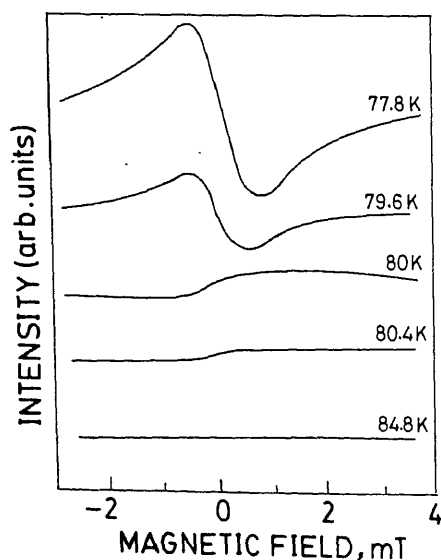


Figure 1. Near-zero-field signal of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ as a function of temperature in the superconducting state.

Immediately following this preliminary report, in a more detailed publication (Bhat *et al* 1987b) the phenomenon was characterized further not only in the microwave range but also in the rf range between 8 and 22 MHz. The fact that the signal occurred centred at zero field for frequencies different by three orders of magnitude indicated that one was essentially dealing with a non-resonant phenomenon. The long hysteretic behaviour dependent on the modulation amplitude observed earlier was confirmed. As a function of decreasing temperature, the intensity of the signal was observed to go on increasing reaching a plateau around 77 K. The temperature dependence was tracked in more detail at rf frequencies and a broadening of the signal as a function of decreasing temperature was observed (figure 2). The signal width was also found to depend upon the particle size. With fine powder samples, a large number of narrow signals with peak-to-peak widths of a fraction of an Oe were observed. In the rf range, the frequency change of the oscillator on going from the normal to the superconducting state was measured and a large increase in the frequency ($\sim 4\%$) was observed. This change was attributed to the diamagnetic response of the sample and the absorption signals were concluded to occur consequent dissipation in the Josephson junctions. Further, a sensitivity of the signal intensity to the presence of oxygen was found. It was observed that the signal intensity was much smaller for an evacuated sample. When exposed to air or oxygen, the intensity built up again. A part of this increase in the intensity could be attributed to better and faster equilibration of temperature. The oxygen or air leads to more effective thermal contact between the grains of the powder sample and also between the sample and the walls of the container kept at 77 K. However, in an experiment carried out (Bhat *et al*, unpublished) to check this aspect where the evacuated sample was kept at liquid nitrogen temperatures for a long time ($\sim 1/2$ h) and then air was let

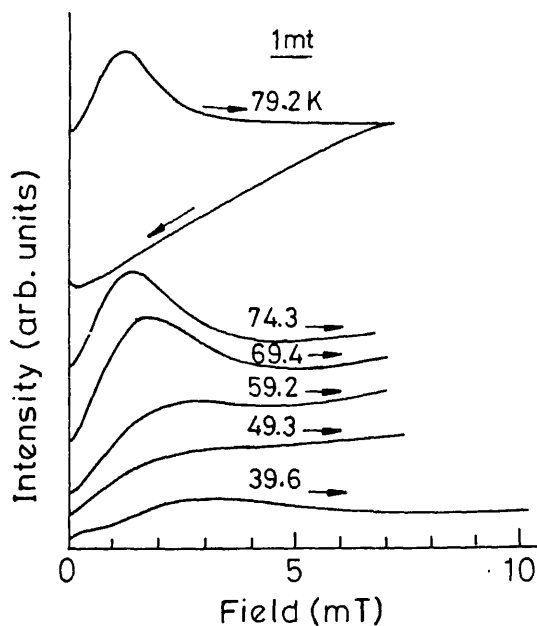


Figure 2. Derivative signals recorded at 13.35 MHz at different temperatures with a CW NMR spectrometer.

in, an increase in the signal intensity was found. It must also be noted that Blazey *et al* (1988), in a subsequent study of machined, then lightly etched and finally anodically oxidized Nb metal, found that the signal disappeared on etching and returned after oxidation.

Shortly after our first report and almost contemporaneously with our second, a large number of studies in the microwave range using the similar technique of the use of an ESR spectrometer were reported and essentially confirmed our major observations (Blazey *et al* 1987; Dulcic *et al* 1987; Durney *et al* 1987; Khachatryan *et al* 1987; Rettori *et al* 1987; Stankowski *et al* 1987; Peric *et al* 1988). In the following pages, we shall discuss some of these various aspects in greater detail after a brief discussion of the experimental techniques used with a view to providing a perspective for understanding the nature of these *non-resonant* signals recorded with the magnetic resonance spectrometers.

3. Experimental techniques

The techniques of EPR (Pilbrow 1990) and NMR (Abragam 1961) are very well established local probe methods which have a history of more than four decades. They have found a wide variety of applications in various fields of science and engineering. There are therefore a large number of textbooks, monographs and treatises available treating the subjects at various levels. A special mention must be made of the book by Poole (1983) on the experimental techniques in ESR which is a very detailed exposition on the subject. In contrast, the practice of CW NMR is almost completely extinct because of the versatility of the pulsed Fourier transform NMR spectrometers. In this context, we may point out that our home-made CW NMR spectrometer enabled us to provide unique experimental results (to be described later) by way of comparison of microwave and rf responses. Excellent description of the experimental aspects of the CW NMR spectrometers is available in a number of earlier books in the field (Andrew 1955).

Even though ESR and NMR differ in the actual techniques because of the different instrumental requirements of the generation and detection of the two frequency ranges differing in three orders of magnitude, they are, however, based on essentially the same phenomenon of observations of the resonant absorption of electromagnetic radiation of appropriate frequency caused by transitions between the Zeeman split energy levels. In the CW EPR and NMR spectrometers the samples placed in either the resonant cavity or the resonant coil of the tank circuit are usually subjected to three different magnetic fields such that the total field H applied to the sample is given by

$$H = H_0 \mathbf{z} + H_1 \cos \omega_1 t \mathbf{x} + H_m \cos \omega_m t \mathbf{z}, \quad (1)$$

where the static field $H_0 \sim 0.5$ T to a few T for NMR, 0.3 T for EPR at X-band, 1.2 T for EPR at Q-band; the resonant frequency $2\pi\omega_1 =$ a few MHz to a few hundred MHz for NMR, 9.5 GHz for X-band EPR, 35 GHz for Q-band EPR; the modulation frequency $\omega_m =$ a few tens of Hz for NMR and usually 100 kHz for EPR. The strengths of H_1 and H_m fields may vary from a fraction of an Oe to a few Oe. As a consequence of the magnetic field modulation and the phase-sensitive detection schemes normally employed in these spectrometers, the signal recorded is in the derivative form. In the

se of an EPR experiment, the response of the sample to these fields is detected as change in the reflected microwave power level resulting from the absorption of the microwaves by the sample on crossing through the resonance consequent to scanning the dc magnetic field. The reflected microwaves are incident on a detector diode which normally operates in the 'linear law' regime and outputs a voltage proportional to the square root of the absorbed microwave power. The CW NMR spectrometers operating in the single-coil configuration normally yield signals which are changes in the rf levels of the tank circuit which can be looked upon as a consequence of a change in the shunt resistance of the circuit on resonance. In both the cases, the signals can be expressed in terms of the quality factor Q of the resonator: i.e. the signal voltage ΔV is given by

$$\Delta V = -V_0 \zeta (4\pi\chi'' + i4\pi\chi')Q, \quad (2)$$

where V_0 is the rf level in the absence of resonance, ζ the filling factor, and χ' the real part of the complex susceptibility of the sample. Since V_0 is real, to first order, only χ'' is detected. The imaginary component $-iV_0Q4\pi\chi'$ is said to be in quadrature and affects the magnitude of the loss only to the second order in χ' . However it can lead to a change in the frequency of the resonator which also can be used to detect it (Bhat *et al* 1987b) and characterize the superconducting state.

Critical current density measurements of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin films by non-resonant absorption method

As mentioned earlier, it is normal practice in the CW EPR and NMR spectrometers to use low-frequency magnetic field modulation and phase-sensitive detection which result in the field derivative of the absorption being recorded. Here we show that this fact can also be used to determine the critical current density J_c of superconducting materials (Srinivasu *et al* 1991). We study thin-film samples of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (23) compound and measure the intensity dependence of the signals on the amplitude of the modulating field and interpret it in terms of the Bean critical state model (Bean 1962, 1964). The effective J_c values thus obtained, when scaled to take into account the recent observations (Baczewski *et al* 1991) that the critical current is sustained primarily by the normal gradient in the in-plane component of the flux density, yield values J_{cs} that compare satisfactorily with independently measured transport J_c values.

The 123 films were fabricated by pulsed laser deposition method. The films were characterized by X-ray diffraction. The resistance was measured by standard four-probe method. Transport J_c measurements were carried out on 80-micron ribbons of the films. The ribbons were made by laser dry-etching of the films using tungsten wire masks.

A home-assembled CW NMR spectrometer based on a Robinson-type level-limited oscillator working at a nominal frequency of 10 MHz was used to record the non-resonant rf response (Bhat *et al* 1987b). Field modulation at 87 Hz was used and the lock-in detection yielded the derivatives of the rf loss signals. The static field H_0 was swept in the region ± 100 Oe. The modulating field amplitude H_{ac} could be varied between 0 and 20 Oe. The signals were recorded at 77 K for various values of the modulating field. H_0 and H_{ac} were collinear and perpendicular to the plane of the film.

Table 1. Transition temperatures T_c , transition widths ΔT , ratios of the resistances at 300 K and 100 K, and the critical current densities J_c determined by rf absorption and transport current method for four 123 films at 77 K.

Film	T_c (K)	ΔT (K)	R_{300}/R_{100}	rf absorption		Transport T_c (A/cm ²)
				J_{eff} (A/cm ²)	J_c	
A	86	2	2.839	0.15×10^2	1.86×10^5	2.3×10^5
B	81	3.6	2.846	0.33×10^2	3.92×10^5	5.8×10^5
C	84	4	2.55	0.34×10^2	4.02×10^5	5.0×10^5
D	81	8	1.879	$> 0.1 \times 10^3$	$> 1 \times 10^6$	not available

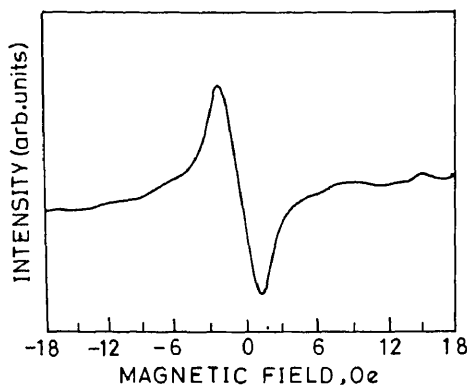


Figure 3. The derivative of the rf loss signal recorded at 77 K for film B.

Now we present our results on four different thin films, designated A, B, C and D for convenience, even though a much larger number of films was fabricated and studied. Table 1 presents for the four films the superconducting transition temperature T_c , the transition widths ΔT , the ratios of the resistances at 300 K and 100 K, R_{300}/R_{100} , and the critical current densities at 77 K determined by the transport current measurement and the non-resonant rf absorption method (to be discussed below). Figure 3 shows a typical non-resonant rf loss signal recorded in the derivative form. The peak-to-peak intensity of the signal was measured as a function of the amplitude H_{ac} of the modulating field. The results are plotted in figure 4. The effects of the modulation amplitude on non-resonant microwave absorption have been studied by several workers (Bhat *et al* 1987b; Blazey and Hohler 1989; Pozek *et al* 1989; Rakvin *et al* 1989). Pozek *et al* (1989) showed that one of the effects of the modulation is to change the fluxon density in the sample. In this sense the modulating field can be considered to be superposed on the static field H_0 , thus rendering the flux density inside the sample time-dependent. Following Bean (1964), the flux density inside the sample can then be written as

$$B = B(H_0) + \sum_{n=1}^{\infty} \alpha_n \sin(n\omega t), \quad (3)$$

with α_1 (the amplitude of the first harmonic) $\propto H_{ac}^2/H^*$ for $H_{ac} \leq H^*$, where H_{ac} is

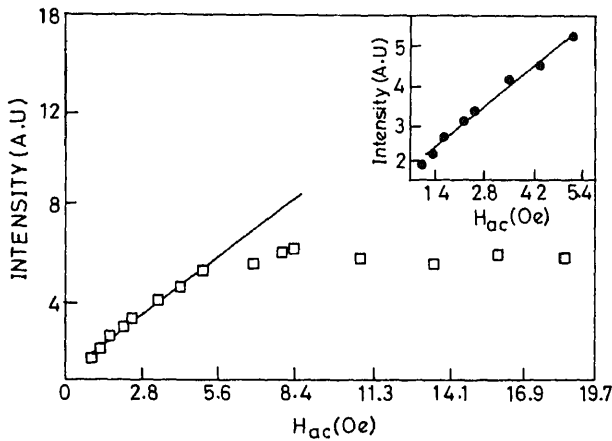


Figure 4. Intensity of the derivative signal as a function of the modulation amplitude for the film marked B in table 1. The inset shows the region of the linear fit expanded.

the amplitude of the ac field and H^* the field value for which the flux penetrates the entire sample. The origin of the rf loss in the case of single crystals and crystalline thin films is essentially in the damped motion of the fluxons (Srinivasu *et al* 1994a).

Therefore the loss

$$S \propto f n, \quad (4)$$

where a fraction f of the fluxon density $n = B/\phi_0$, with ϕ_0 the elemental flux quantum, is considered to be free. Therefore

$$S = f[B(H_0) + \frac{H_{ac}^2}{H^*} \sin(\omega t) + \text{higher harmonics}]. \quad (5)$$

In this expression, the first term represents the dependence of the general lineshape, hysteresis and flux trapping with respect to the dc field. The second term contains the information on the modulation effects.

The maximum loss $S_{\max}$ in a modulation cycle, therefore, will be proportional to $(H_{ac} + H_0)^2/H^*$. Since, in our experiment, consequent to lock-in detection, the derivative of the loss is recorded and therefore,

$$\frac{dS}{dH} \propto \frac{2(H_{ac} + H_0)}{H^*}. \quad (6)$$

Therefore, if the modulation amplitude H_{ac} is increased starting from a small value, until H^* we expect a linear dependence of the recorded signal intensity on H_{ac} . For $H_{ac} \geq H^*$, as shown by Bean, there will be a departure from the quadratic dependence of the first harmonic on H_{ac} resulting in the departure of the signal intensity from linearity. This is what is observed in our experiments as shown in figure 4.

Obviously, the field value for which the departure occurs corresponds to H^* . Following Bean again,

$$H^* = \frac{\pi J_c D}{5}, \quad (7)$$

where D is the thin film width. J_c can be calculated using this relation. However, this J_c is only an effective J_c and not the true J_c for the following reason.

As shown by Baczewski *et al* (1991), in calculating J_c from the relation

$$\nabla \times H = \frac{4\pi J_c}{c} = \frac{\partial H_D}{\partial z} \frac{\partial H_z}{\partial D}, \quad (8)$$

for thin-film geometry, the term $\partial H_D/\partial z$, i.e. the gradient of the radial field along the axial direction z is the dominant one rather than the term $\partial H_z/\partial D$ used for calculating the J_{eff} above. The term $\partial H_D/\partial z$ is shown to exceed the $\partial H_z/\partial D$ by a ratio of order D/t where t is the thickness of the sample. Therefore the true J_c is obtained by multiplying the J_{eff} by this factor. Table 1 lists values of J_{eff} and J_c and also J_{cs} determined by the transport current method. As can be seen from the table, the consistency between the J_{cs} determined by the non-resonant rf absorption technique and the transport current method is quite satisfactory.

5. Distinction between weak link and bulk responses

One of the characteristic features of the high- T_c superconductors is the hierarchy of weak links they contain. These weak links are comprised mainly of the grain boundaries in dense powders and compact sintered pellets, whereas in isolated grains and well-annealed single crystals they originate in the twin boundaries (when present, like in the 123 crystals). In fact it is possible that due to the very short coherence length characterizing these materials, point defects, oxygen vacancies and even the insulating layers in between the conducting planes can act, in certain respects, like weak links, as originally suggested by Deutscher and Muller (1987). Then, since the lower critical field H_{c1} of the weak links is orders of magnitude smaller (~ 0.1 Oe) than that of the bulk, the magnetic field penetration is more facile into the junctions than into the bulk material. The critical current through the junctions then becomes dependent on the field according to the well-known diffraction relation $J_c = J_c(0) [\sin(H/H_0)/(H/H_0)]$, where the symbols have their conventional meanings, and thus can lead to the observed field-dependent absorption (Dulcic *et al* 1989a). In fact, this model has been proposed and successfully adapted to explain the low-field absorption behaviour by many workers (Dulcic *et al* 1989b; Owens 1990; Puri *et al* 1990). However, it is also possible when the size of the junction d is such that $d > \lambda_L$ (where λ_L is the London penetration depth) fluxons are nucleated within the weak links and their viscous motion will result in dissipation. This model was proposed by Portis *et al* (1988) to explain the low-field absorption in pellet samples.

It has been realized that to distinguish between these two different possible origins of the non-resonant microwave absorption signals is not easy (Dulcic *et al* 1989c). Further, the contribution to the dissipation from the Abrikosov fluxons and from the fluxons nucleated in the intragranular weak links (twin boundaries, insulating layers in the structure, and the like), if any, also need to be delineated. Here we show that studying the non-resonant absorption at widely different frequencies can help decide between the diffraction effect and the viscous fluxon motion as the possible causes of dissipation. We have studied the YBCO superconductor in two different forms, namely epitaxially grown thin films and sintered pellets, in both the microwave (9.1 GHz) and radio (19.5 MHz) frequency ranges. We observe characteristic depen-

dence of the lineshapes on frequency and the nature of the samples, from which we conclude that close to T_c in the thin-film and the sintered-pellet forms the lineshapes are more consistent with the model of dissipative fluxon motion and not that of the diffraction effect. While there have appeared a large number of reports on the study of non-resonant absorption using EPR spectrometers there are hardly any such measurements in the rf range [apart from the early report of Bhat *et al* (1987b), the only other work appears to be Orlandi and Rigamonti (1991)]. We show (Srinivasu *et al* 1994a), for the first time, how a comparative study covering the two frequency ranges can give insight into the microscopic origin of the dissipative processes. For a taste of the rich panorama of the properties of the high- T_c superconductors as revealed by the method of non-resonant electromagnetic response the reader is referred to some of our other publications (Bhat *et al* 1991, 1994; Srinivasu *et al* 1994b).

The sintered pellets of the YBCO samples used were prepared by the conventional solid-state method. The thin films of the same were prepared by the pulsed laser deposition technique as described in Hwang *et al* (1989). The films were deposited on SrTiO₃ (100) substrates (kept at $\sim 740^\circ\text{C}$) and had the c axis perpendicular to the plane of the film. Thickness of the films was measured to be $\sim 2500 \text{ \AA}$. A four-probe resistivity measurement indicated a T_c of 87 K with the transition width of $\sim 2 \text{ K}$. The critical current density J_c was estimated to be $\sim 5 \times 10^5 \text{ A/cm}^2$ at 77 K showing that the film was of moderately good quality. An optical polarizing microscope examination showed that similarly prepared films were free from intergranular boundaries though twin boundaries were present. It may further be noted that films prepared following the same method and with $J_c \sim 7.5 \times 10^5 \text{ A/cm}^2$ have earlier been shown to be free from intergranular junctions (Hwang *et al* 1989).

The non-resonant absorption experiments in the microwave range were carried out with a Varian E109 X-band EPR spectrometer operating at a nominal microwave frequency of 9.1 GHz, using mostly 100 kHz field modulation and phase-sensitive detection. It is well known (Bhat *et al* 1987b; Blazey and Hohler 1989; Pozek *et al* 1989; Rakvin *et al* 1989) that in the low-modulation regime ($\sim 0.05 \text{ Oe}$) the signals are dominated by the modulation of the boundary currents, giving rise to opposite phases of the signals for forward and reverse magnetic field sweeps. However, at higher modulation amplitudes, the magnetic flux density gets modulated, resulting in signals which are true derivatives of the absorption. Therefore the modulation amplitude in our experiments was fixed at 4 Oe for all the experiments ensuring that the modulation amplitude-dependent hysteresis and phase reversal do not complicate the results. For the modulation amplitudes used in these experiments, we are in the regime where the signal intensity is proportional to the modulation amplitude. It was checked and confirmed that the signal shapes are not distorted at this and even a slightly higher (5 Oe) value of the modulation amplitude. A microwave power of $\sim 22 \text{ mW}$ is used throughout. For the experiments in the rf range, a home-made (CW) NMR spectrometer (Bhat *et al* 1987b) operating at a nominal frequency of 19.5 MHz was used. Fixed modulation of 4 Oe at a frequency of 87 Hz and phase-sensitive detection were used.

In both the microwave and rf ranges the experiments were carried out at 77 K, by directly immersing the samples in liquid nitrogen. All the recordings were done with the ab -plane of the film perpendicular to the static field (i.e. $H \parallel c$). The magnetic field was mostly scanned between -50 Oe and $+50 \text{ Oe}$ thus eliminating any scan range-dependent phase reversal and hysteresis or other artifacts (however, see below).

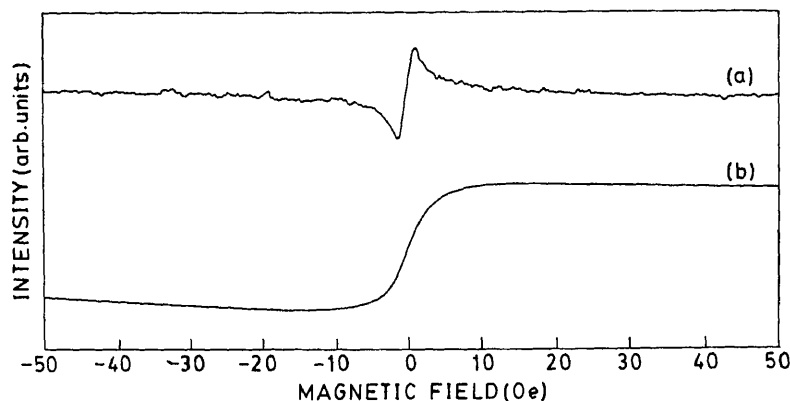


Figure 5. Field derivative of the non-resonant absorption signals for the YBCO thin film at (a) 19.5 MHz and (b) 9.1 GHz. To be noted is the drastic difference in the lineshapes at the two frequencies.

With these experimental conditions, the forward and backward sweeps of the static magnetic field produced almost reversible derivative absorption signals in both the microwave and rf ranges for $H \perp ab$ -plane of the film. Figure 5 presents the field derivatives of the non-resonant absorption signals recorded at 19.5 MHz and 9.1 GHz for the thin-film samples. The line shapes are seen to be quite different in the two cases. Derivative-like signals reaching the baseline at a static field ~ 20 Oe indicating a saturation of the field-dependent absorption at low static fields are observed in the rf range, whereas in the microwave range the signals do not come back to the baseline until at much higher fields, proceeding almost in a parallel fashion to the field axis at low fields. Usually, the magnetic field is modulated at a frequency of 100 kHz in commercial EPR spectrometers while we had used 87 Hz for the experiments in the rf range. To eliminate the possibility of the observed difference in the lineshapes arising due to the difference in the modulation frequency, experiments were carried out using 87 Hz as the modulating frequency with the EPR spectrometer. No difference in the lineshape from that obtained with 100 kHz modulation was observed establishing that the difference in the lineshapes is not due to the difference in the modulation frequencies. In figure 6 we show signals from thin-film and pellet samples recorded at 9.1 GHz. It is seen that while in the case of the thin film the signal does not saturate until very high fields (1–2 kOe) (results not shown), in pellet samples they saturate at much lower (20 Oe) fields. Such absorption signals in the microwave range extending to large fields, similar to our observation in thin films, were earlier observed in YBCO single crystals in a small temperature range just below T_c by Dulcic *et al* (1988) (see the 'A' type signals in their figure 1). Further, these signals also were shown to have no hysteresis and therefore were true derivatives of absorption. Similar signals were reported by Buluggiu *et al* (1991) in compact sintered pellets of YBCO and bismuth 2212 samples and by Kataev *et al* (1991) in bismuth 2212 samples. The results of Marcon *et al* (1991) on the field dependence of non-modulated microwave absorption in YBCO sintered pellets are also similar. An important conclusion coming from these various studies is that the microwave absorption goes on increasing with the magnetic field up to high fields in sintered compact pellets and isolated powders, but

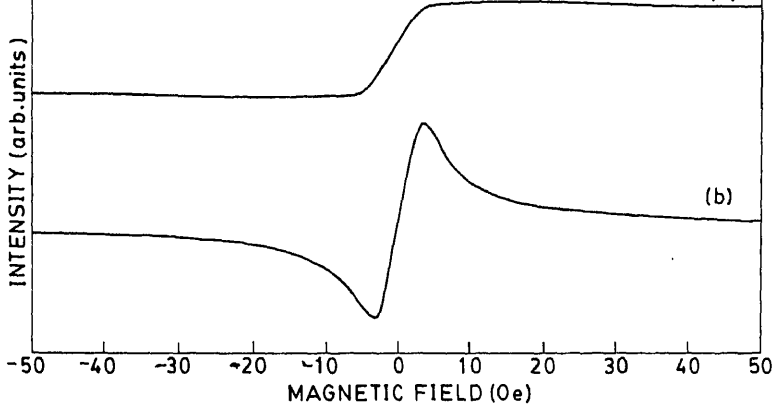


Figure 6. Field derivative of the non-resonant microwave absorption signal ($\omega = 9.1$ GHz) for (a) the YBCO thin film and (b) the YBCO pellet.

saturates at very low fields of the order of 10–50 Oe in loosely packed pellets and powders that are not crushed to submicron size and are not isolated from each other.

Dulcic *et al* (1989a) attribute their type A signals in single crystals to the microwave loss arising due to the diffraction reduction of junction currents J_c in twin boundaries because of the applied magnetic field. According to this model the power absorbed in the junction, P , takes the form

$$P = P_n \frac{1}{1 + \eta_D},$$

where $P_n = (1/2)I_{mw}^2 R$ is the absorption when the junction is driven normal. I_{mw} is the microwave current, R the junction resistance, and

$$\eta_D = \eta_0 F^2(H),$$

where η_0 is the value of the parameter η at zero magnetic field. $F(H)$ is the value of the reduction factor $[\sin(H/H_0)]/(H/H_0)$ averaged over all junctions and $H_0 \approx (\phi_0/\mu d L)$, where μ is the permeability, and $d = 2\lambda_L + t$ for a junction of thickness t and length L . Thus in this model, the junction supercurrent decreases as the applied magnetic field increases leading to an increase in the microwave absorption. The field H_0 at which the absorption saturates is seen to depend upon the junction dimensions. Following the above model, Dulcic *et al* (1989a) explain the large saturation fields (~ 1 –3 kOe) observed for their type A signals as originating in the junctions formed by the twin boundaries of dimensions 10^3 – 10^4 Å. Our experimental results show that for the thin-film sample of YBCO, microwave absorption at 9.1 GHz does not saturate until the applied fields reach values as high as ~ 1 kOe, whereas at 19.5 MHz the absorption saturates at very low fields (~ 20 Oe) as shown in figure 5, with all the other experimental conditions remaining the same. Therefore the model used by Dulcic *et al* (1988), where the saturation field depends upon the weak-link dimensions, cannot explain this result where just by changing the frequency from 9.1 GHz to 19.5 MHz

we see saturation fields differ by orders of magnitude. The expected frequency dependence of absorption from the Dulcic model (figure 2b of Dulcic *et al* 1989a) is in fact opposite to our observations, i.e. according to the model of the microwave absorption originating in the diffraction effect, the width of the absorption decreases with increasing frequency, whereas we find experimentally that in the rf (19.5 MHz) range, the derivative of the absorption signal is narrow and by increasing the frequency to microwave range (9.1 GHz), the signal width increases (figure 5). Therefore we believe that in the small temperature range below T_c , the field dependence of the microwave absorption in single crystals and single-crystalline YBCO films does not arise because of the diffraction effect, but, as will be shown below, because of the damped motion of free fluxons. We show that the large frequency dependence of the lineshape observed experimentally follows from this model, which was earlier used by Portis *et al* (1988).

Firstly, the near absence of hysteresis both in the microwave and the radio frequencies suggests that we are almost completely in the flux flow regime. It may be mentioned that earlier Marcon *et al* (1991) attributed this kind of hysteresis-less signals near T_c to flux flow. In such a situation we are justified in taking $B \sim H$. Then, the surface resistance R arising from the damped motion of the fluxons is given by

$$R = (X_0/\sqrt{2})(-1 + (1 + 4(f/B_0)^2 B^2)^{1/2})^{1/2}, \quad (9)$$

where $X_0 = [4\pi\omega\mu\lambda_L/c^2]\mu^{1/2}$ is the impedance at zero magnetic field, B the flux density, and f the fraction of free fluxons. The permeability μ , defined by the relation $B = \mu H$, is ~ 1 and ω is the frequency of the electromagnetic radiation. The fraction of free fluxons f was taken by Portis *et al* to be ~ 0.1 . However, in the flux flow regime, as obtained in our experiment, one can reasonably assume that all the fluxons are free and therefore $f \sim 1$. Further, in (9) B_0 is given by

$$B_0 = 8\pi\omega\mu\eta\lambda_L^2/\phi_0, \quad (10)$$

where η is the coefficient of viscosity, ϕ_0 the elementary flux quantum, λ_L the London penetration depth, and μ the permeability taken to be ~ 1 as explained above. With this, B_0 can be written as

$$B_0 = 8\pi\omega\eta\lambda_L^2/\phi_0,$$

and thus essentially depends on the frequency, the viscosity coefficient and the penetration depth. Since at 77 K both rf and microwaves penetrate the thin film (of thickness ~ 2500 Å) fully, λ_L , which is the same for both the frequency ranges (estimated (Krusin-Elbaum *et al* 1989) to be ~ 2000 Å at 77 K) does not alter the conclusions regarding the frequency dependence of the lineshapes of the signals from a given film. Therefore a change in either ω or η changes B_0 . By plotting (9) for different values of f/B_0 , (in our case $f \sim 1$), i.e. essentially for different values of B_0 , we can see from figure 7 that the derivative of absorption vs field shows different characteristics observed experimentally. In this figure with the dc field swept between -50 Oe and $+50$ Oe, the field derivative of the absorption is plotted for different B_0 values ranging from 10 Oe to 1000 Oe. One can observe clearly that for small values of B_0 of the order of ~ 10 Oe, the absorption signals saturate quickly, whereas for $B_0 = 1000$ Oe, the signal does not saturate at low fields. Experimentally, for a

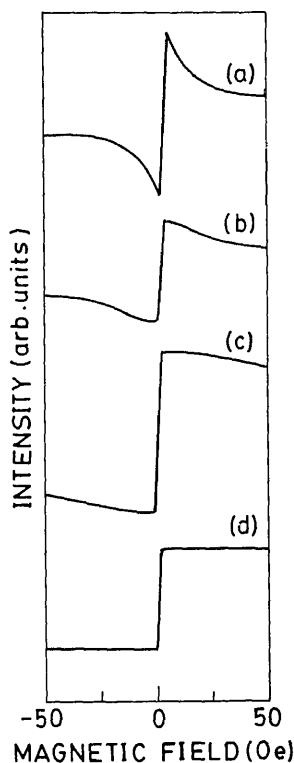


Figure 7. Simulation of the field derivative of the non-resonant absorption signals for different values of B_0 : (a) 10 Oe, (b) 30.3 Oe, (c) 100 Oe and (d) 1000 Oe.

given sample with a certain η different values of B_0 are realized by changing the operating frequency. As mentioned earlier, in our experiment we have recorded the signals at 9.1 GHz and 19.5 MHz. The corresponding spectra shown in figure 5 in the derivative form were taken at the same temperature and with field sweeps of ± 50 Oe. One can see that at 19.5 MHz the signal saturates at ~ 20 Oe, whereas at 9.1 GHz it does not saturate at low fields. These experimentally observed derivative absorption lineshapes at the two widely different frequencies can be simulated using (9), with appropriate B_0 values, e.g. $B_0 \sim 1$ Oe for rf and 150 Oe for microwave frequency. Figure 7 shows such simulation for the rf range. For this simulation we have used $\omega = 19.5$ MHz, $\lambda_L \sim 2000$ Å (Krusin-Elbaum *et al* 1989) and $B_0 = 1$ gauss which gives $\eta \sim 0.878 \times 10^{-6}$ cgs units. This value of η is quite high and rules out any grain-boundary effects following Portis and Blazey (1985), who argue that grain-boundary viscosity coefficient is of the order of 10^{-13} cgs units. The high viscosity coefficient obtained by us which is comparable with the bulk values suggests that the low-field microwave absorption in our thin-film samples is coming from the bulk. Recently Kataev *et al* (1991) showed that in very compact pellets signals saturate at high fields as in the case of single crystals and thin films. One can understand this result in the following way: in a compact pellet, flux squeezing effects (Dulcic *et al* 1989c; Orlandi and Rigamonti 1991) dominate and even low applied fields can enter into grains due to these effects. Once flux enters into the grains, one would see

intragranular effects which would again make the signals look similar to those in films and single crystals.

Another possibility that needs to be considered is that of the intrinsic weak links (Deutscher and Muller 1987; Dulcic *et al* 1988, 1989c) present even in single crystals and single-crystalline thin films. Some of these weak links can conceivably have superior qualities like high values of η showing microwave absorption signals similar to that of the bulk. But recent magnetization measurements on thin-film (Yeshurun *et al* 1990) as well as single-crystal (Tamegai *et al* 1992) samples show the applicability of Bean's critical-state model for these cases ruling out granularity even on the scale of the twin boundaries. Another important point about the losses due to damped motion of free fluxons in a weak link is that the weak link size should be larger than the fluxon size, so that the fluxon can move inside the weak link. Certain defects like point defects and oxygen vacancies cannot contribute to this mode of loss because the fluxons cannot move inside such defects and therefore such defects can only act as pinning centres. On the basis of all these considerations it seems very likely that the microwave absorption in our thin-film samples which saturates at high magnetic fields has its origin in the motion of the fluxons in the bulk of the material.

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Growth and applications of superconducting and nonsuperconducting oxide epitaxial films

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Abstract. Growth and characterization of high-temperature-superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ and several metallic-oxide thin films by pulsed laser deposition is described here. An overview of substrates employed for epitaxial growth of perovskite-related oxides is presented. Ag-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$ films grown on bare sapphire are shown to give $T_c = 90$ K, critical current $> 10^6$ A/cm² at 77 K and surface resistance = 450 $\mu\Omega$. Application of epitaxial metallic LaNiO_3 thin films as an electrode for ferroelectric oxide and as a normal metal layer barrier in the superconductor-normal metal-superconductor (SNS) Josephson junction is presented. Observation of giant magnetoresistance (GMR) in the metallic $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ thin films up to 50% is highlighted.

Keywords. Epitaxial thin films; metallic oxides; high- T_c films; SNS junction; LaNiO_3 ; $\text{La}_{1-x}\text{Pb}_x\text{MnO}_3$; ferroelectric oxides; ferromagnetic oxides.

Introduction

Since the discovery of superconductivity at high temperature in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (Bednorz and Muller 1986) and subsequently in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($T_c = 90$ K) (Wu *et al* 1987), extensive efforts have been made to fabricate thin films of these materials because of the high possibility of their use in electronic devices. Even though a large number of Bi- and Tl-based oxides are known to give superconducting transition temperature $T_c > 90$ K, the majority of efforts in the thin-film area still continue to be on the growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) films because of the relative ease with which YBCO films can be fabricated *in situ* with correct composition. Further, thin films give high critical current density (J_c) routinely at 77 K. Chaudhari *et al* (1987) were the first to show that J_c as high as 10^6 A/cm² can be achieved in epitaxially grown YBCO films on $\langle 100 \rangle \text{SrTiO}_3$ (STO) substrates. Pulsed laser deposition (PLD) is the most successful technique among the commonly used methods to fabricate good quality high- T_c thin films. PLD has also been extended to grow a variety of epitaxial nonsuperconducting oxide thin films for superconductor-insulator-superconductor (SIS) and superconductor-normal metal (metallic oxide)-superconductor (SNS) trilayer heterojunctions. These types of multilayer structures are required to realize Josephson junctions for superconducting quantum interference device (SQUID) fabrication.

The fabrication of trilayer junctions using YBCO films as superconductor and $\text{PbBa}_2\text{Cu}_3\text{O}_7$ (PBCO) as insulating barrier was reported for the first time by Rogers *et al* (1989). The trilayer junction fabricated by them did show Josephson-junction (I - J) behaviour, but the current (I)-voltage (V) characteristic of the junction was unlike the I - V characteristic of SIS junction fabricated out of the classical superconductors and insulating barriers such as $\text{Nb-Al}_2\text{O}_3$ -Nb. Subsequent attempts to make SIS

junctions using other insulating layer like NdGaO_3 or NdAlO_3 also showed only the SNS type of I - V characteristics. Therefore attempts were made to fabricate SNS Josephson junctions with perovskite-related metallic oxides as the N-metal barrier layer (Char *et al* 1993). Thus fabrication of epitaxial thin films of perovskite-related metallic oxides itself became an important aspect of research in conjunction with high- T_c oxides. Further, perovskite-related metallic oxides could also be used as electrodes for ferroelectric oxide capacitors. Another advantage of epitaxial oxide thin films was that they are essentially single-crystal-like materials and unusual properties such as giant magnetoresistance (GMR) in lanthanum manganates could be realized (Searle and Wang 1970).

Realizing the importance of this area of research, we have set up a PLD system (Dijkkamp *et al* 1987; Inam *et al* 1988; Srinivasu *et al* 1991) in our laboratory to fabricate high-temperature-superconducting and related oxide thin films. In this article, we will present an overview of the substrates employed for epitaxial growth of perovskite-related oxide thin films and some of the recent results that we have obtained on (a) Ag-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Ag-YBCO) thin films, (b) fabrication of epitaxial metallic LaNiO_3 thin films, (c) fabrication and properties of YBCO/ LaNiO_3 /YBCO trilayer junctions, (d) LaNiO_3 thin-film electrodes for $\text{Bi}_2\text{VO}_{5.5}$ ferroelectric oxide, and (e) giant magnetoresistance in epitaxial $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ thin films.

2. Experimental

The PLD experiments for the growth of $\text{YBa}_2\text{Cu}_3\text{O}_7$, LaNiO_3 and other related oxide films were carried out using KrF ($\lambda = 248$ nm) excimer laser with a 300 mm focal length quartz lens for focusing the laser beam. The excimer pulse had maximum energy of 1000 mJ with a pulse width of 25 ns and 1–10 Hz of variable repetition rate. The laser fluence was varied from 1.5 to 2.5 J/cm² by varying the laser pulse energy and quartz attenuators. A schematic diagram of the experimental set-up is given in figure 1. For thin-film deposition, the substrates were held on the surface of the heater face plate by Ag paste and the temperature on the surface of the heater was measured using a chromel–alumel thermocouple fixed onto it by Ag paste. The temperature difference between the heater face plate and the substrate top surface was about 30–40°C which was calibrated by fixing another thermocouple on the top surface of substrate. The oxygen pressure during film deposition was maintained at about 200–450 m torr depending on the material. The deposition temperature was optimized separately for each material, and it was about 780°C for YBCO. The growth and structural properties of high-temperature-superconducting oxide and other oxide films have been reported in detail in our earlier publications (Srinivasu *et al* 1991; Hegde *et al* 1993, 1994; Satyalakshmi *et al* 1993; Prasad *et al* 1993).

The YBCO/LNO/YBCO trilayer structure was fabricated by depositing YBCO film first on the complete surface of STO and subsequently depositing LNO on the previously deposited YBCO film by masking one side of the film by silver foil. This was followed by the deposition of YBCO on the central region of LNO by masking the remaining portion with silver foil. The structural characterization of all the individual films as well as of the trilayer was carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). The conductivity measurements were carried out by a four-probe method

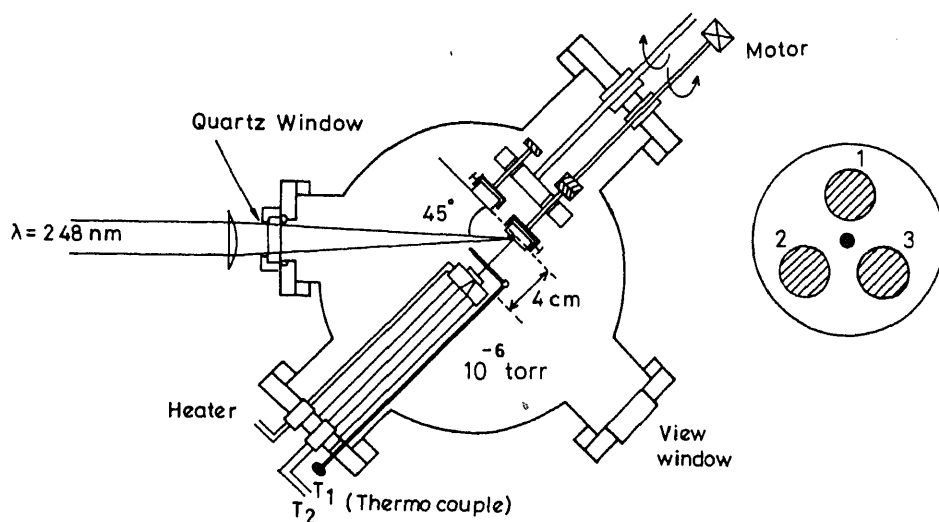


Figure 1. Triple target pulsed laser deposition system.

and the I - V characteristics of the trilayer were determined using laser-patterned microbridges.

3. Substrates for epitaxial growth of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) and related oxide films

As mentioned earlier, the breakthrough to realize high T_c , and high J_c came only when the YBCO epitaxial thin films were grown on SrTiO_3 (100) single-crystal substrate by Chaudhari *et al* (1987). Ability to grow *in situ* YBCO films in the *ex-situ* deposited condition giving T_c 90 K by introducing oxygen during the deposition was a significant step towards the use of YBCO films for high- T_c applications (Inam *et al* 1988). A large number of single-crystal substrates have been employed to fabricate YBCO and other oxide films. YBCO has the lattice parameters $a = 3.83 \text{ \AA}$, $b = 3.89 \text{ \AA}$ and $c = 11.65 \text{ \AA}$. General criteria for the epitaxial growth of these high- T_c oxide films are summarized below:

- (i) The substrate should have structural compatibility, i.e. possess cubic and perovskite-related structure.
- (ii) The lattice parameter of the substrate should be within 5% of the lattice parameters of high- T_c oxides.
- (iii) These substrates should have thermal expansion coefficients close to that of YBCO itself. Otherwise, due to thermal shock during cooling, the grown films are known to develop microcracks leading to discontinuity in the films.
- (iv) The substrate should be chemically and structurally stable at the processing temperature of YBCO, which is generally around 750–800°C.
- (v) The substrate material should be chemically compatible in terms of the nature of chemical bond.

In table 1, we summarize the structure, lattice parameters, thermal expansion coefficient and dielectric constant of a variety of substrate materials. The single crystals

Table 1. Structure, lattice parameters and physical properties of substrates for epitaxial growth of $\text{YBa}_2\text{Cu}_3\text{O}_7$ thin films.

Substrate material	Crystal structure	Lattice parameters ($\text{\AA}$)	Thermal expansion coefficient ($10^{-6}/\text{K}$)	Dielectric constant
SrTiO_3	Cubic (perovskite)	$a = 3.905$	9.4–10.8	7300
LaGaO_3	Orthorhombic (distorted perovskite) (GdFeO_3)	$a = 5.482$ $b = 5.526$ $c = 7.78$ (* $a_0 = 3.892$)	10.6	25
LaAlO_3	Rhombohedral (distorted perovskite)	$a = 5.364$ $c = 13.11$ ($a_0 = 3.788$)	10	16
YSZ	Cubic (fluorite)	$a = 5.16$ ($a_0 = 3.65$)	9.2–10.3	27
MgO	Cubic (NaCl)	$a = 4.212$	13.8	14
Al_2O_3 (sapphire)	Trigonal	$a = 5.14$ ($a_0 = 3.64$)	5	10
Si	Diamond	$a = 5.43$ ($a_0 = 3.83$)	6.7	12
KTaO_3	Cubic (perovskite)	$a = 3.989$	—	—
BaTiO_3	Tetragonal (perovskite)	$a = 3.99$ $c = 4.03$	19	> 2000
LaSrGaO_4	Tetragonal (K_2NiF_4)	$a = 3.843$ $c = 12.861$	—	—
$\text{Y}_3\text{Fe}_5\text{O}_{12}$	Garnet	$a = 12.376$ ($a_0 = 4.125$)	—	—
YbFeO_3	Orthorhombic (GdFeO_3)	$a = 5.36$ $b = 5.50$ $c = 7.77$ ($a_0 = 3.86$)	—	4–5
$\text{BaFe}_{12}\text{O}_{19}$	Barium orthoferrite	$a = 5.88$ $c = 23.22$ ($a_0 = 4.158$)	—	—
MgAl_2O_4	Cubic Spinel	$a = 8.059$ ($a_0 = 4.029$)	76	—
$\text{YBa}_2\text{Cu}_3\text{O}_7$	Triple Perovskite	$a = 3.83$ $b = 3.89$ $c = 11.65$	12	—

* a_0 , Pseudocubic parameter

of these materials have been employed to grow epitaxial thin films of YBCO. Single crystals of these materials cut in the $\langle 100 \rangle$ direction generally support c -axis growth. Thus $\langle 100 \rangle$ surface of the substrate supports epitaxial growth, the a - b plane of YBCO aligned parallel to $\langle 100 \rangle$ of the substrate. Some of these substrates are also used for the growth of perovskite-related metallic and ferroelectric oxide thin films.

Among these materials, SrTiO_3 (STO) is a widely used substrate for the growth of YBCO and it is known to give the highest critical current density (10^6 A/cm^2 at

77 K) for epitaxial YBCO films. This is due to the very small lattice mismatch between YBCO and STO. STO is a good lattice-matched substrate, but due to the large dielectric constant, the films grown on this substrate are not good for microwave applications. LaAlO_3 (LAO) single crystal is a commonly used substrate because it is relatively less expensive and high- J_c , 90 K YBCO films on LAO are routinely grown. LaGaO_3 is the best known substrate for YBCO thin-film growth but it is not readily available and it is expensive. Both MgO and YSZ are relatively less expensive but both have about 5% lattice mismatch with reference to YBCO because of which growing high-quality YBCO film is difficult compared to the films on SrTiO_3 . Al_2O_3 (sapphire) is the best-suited substrate for microwave applications. But due to the large lattice mismatch and Al diffusion into YBCO at high temperature making YBCO nonsuperconducting, it is difficult to grow high- J_c , high- T_c YBCO films on sapphire. However, high-quality YBCO thin films have been successfully grown on sapphire by employing a yttria-stabilized zirconia (YSZ) barrier layer on Al_2O_3 . This minimizes the interaction between YBCO and Al_2O_3 . We have grown Ag-doped YBCO on bare sapphire with excellent T_c (90 K) and J_c (10^6 A/cm^2). The results are presented here in the next section.

Silicon is a unique material. There is a famous saying at IBM Laboratories: 'If one can use Si for any electronic applications, don't use any other!' But due to the large thermal mismatch and also the weaker bonding between covalent silicon lattice and the ionic oxides, growth of YBCO on bare silicon has not been successful so far. However, with $\text{MgAl}_2\text{O}_4/\text{BaTiO}_3$ oxide layers as buffer layers on Si(100), the growth of YBCO, with $T_c = 85 \text{ K}$, coated with these buffer layers has been achieved (Wu *et al* 1989).

LaSrGaO_4 is an important substrate material for the growth of *a*-axis-oriented YBCO films. This is one of the important single-crystal substrates which supports high-quality *a*-axis growth of YBCO without any template buffer layer. It is important to note that oxides which are magnetically ordered, such as garnets and orthoferrites are also known to support the epitaxial growth of YBCO with T_c as high as 90 K (Ramesh *et al* 1989). Spinel such as MgAl_2O_4 are also found to be good lattice-matched material for the growth of YBCO, but it has been mainly used as a material for buffer layer. Search for new substrates, new barrier-layer materials and substrates for *a*-axis-oriented growth against *c*-axis-oriented growth of YBCO is still an active area of research.

4. Results and discussion

4.1 Ag-doped YBCO films on sapphire

High-quality epitaxial YBCO films with *c*-axis perpendicular to the (100) cut substrate plane can be characterized by the slope of R vs T curve. If R_{300}/R_{100} is greater than 3, T_c of 90 K and J_c around 10^6 A/cm^2 at 77 K are generally obtained.

Sapphire is the most important substrate which has extremely low loss in the microwave region. High- T_c films in the form of strips are used as transmitting lines without loss in the microwave region. However, growing high-quality, high- J_c , 90 K YBCO films having low surface resistance is difficult on bare sapphire due to the large lattice mismatch and chemical interactions of Al with YBCO. We have overcome

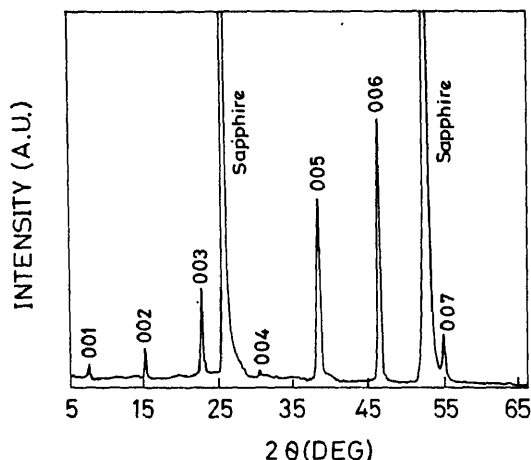


Figure 2. CuK θ - 2θ scan of 7%-Ag-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$ films on sapphire.

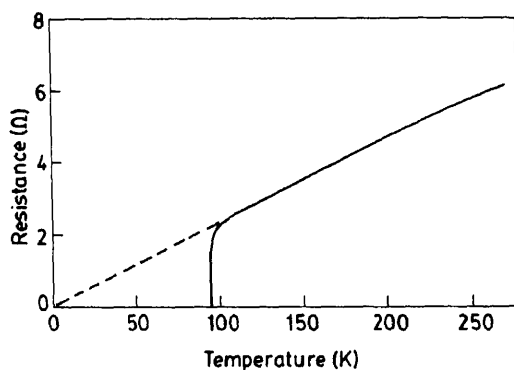


Figure 3. R vs T plot of the above film showing $R_{300}/R_{100} \sim 2.9$ and $T_c = 90$ K.

this problem by growing 7%-Ag-doped YBCO films on bare sapphire. Silver addition lowered the growth temperature from 780°C to 730°C in the PLD system. A typical c -axis-oriented Ag-doped film grown on sapphire is shown in figure 2. Figure 3 shows R vs T plot of Ag-doped YBCO films. The film showed T_c of 90 K. R_{300}/R_{100} was about 2.9. Transport critical current of these films was about 1.2×10^6 A/cm² at 77 K. Microwave surface resistance of Ag-doped films was about 450 $\mu\Omega$ at 10 GHz at 77 K. The T_c , J_c values of Ag-doped YBCO films on bare sapphire reported here are the highest and surface resistance value is the lowest compared to values reported in the literature. Details of the study will be published elsewhere (Dhananjay Kumar *et al*, to be published). We are now using these high- T_c , Ag-doped YBCO films for microwave applications.

4.2 Metallic LaNiO_3 thin films

Metallic oxide films are finding application as the normal metal barrier in the SNS-type Josephson junctions, and electrodes for superconducting, insulating and ferro-

electric oxides. Among the perovskite-related oxides, we have found that LaNiO_3 (LNO) is perhaps the best material for these applications (Hegde *et al* 1994). Epitaxial LaNiO_3 thin films have been routinely grown in this laboratory on a variety of substrates such as LaAlO_3 , SrTiO_3 , MgO , YSZ, $\text{SiO}_2/\text{Si}(100)$ and Al_2O_3 . Typical R vs T plots of a few films are given in figure 4. Resistivity of these LaNiO_3 films is of the order of $300\text{--}400\ \mu\Omega\cdot\text{cm}$. We have grown (100)-oriented LaNiO_3 thin films on $\text{SiO}_2/\text{Si}(100)$ substrate for the first time even though SiO_2 layer on $\text{Si}(100)$ is amorphous. The reason for an oriented growth of LaNiO_3 on amorphous SiO_2 is not clear to us. The θ - 2θ scan of LaNiO_3 over YBCO films is shown in figure 5. Observation of only (100) and (200) LaNiO_3 lines on the epitaxial YBCO films on LaAlO_3 (100) indicates epitaxial growth of LNO on YBCO. The contact conductance between metallic LaNiO_3 and superconducting YBCO thin films has been measured by a modified four-probe method and the value is $1.4 \times 10^4\ \text{ohm}^{-1}\text{cm}^{-2}$ at 77 K, which is about the same as that of Ag and Pd with YBCO films.

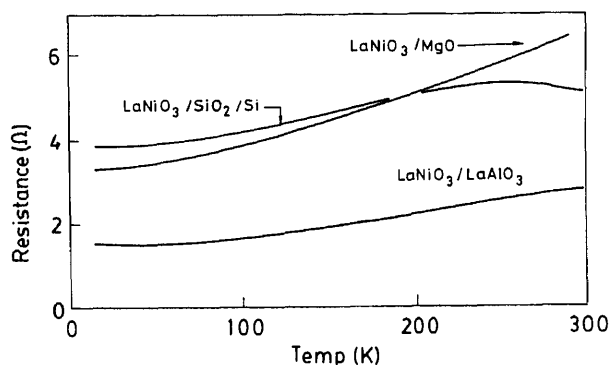


Figure 4. R vs T plot of LaNiO_3 films on different substrates.

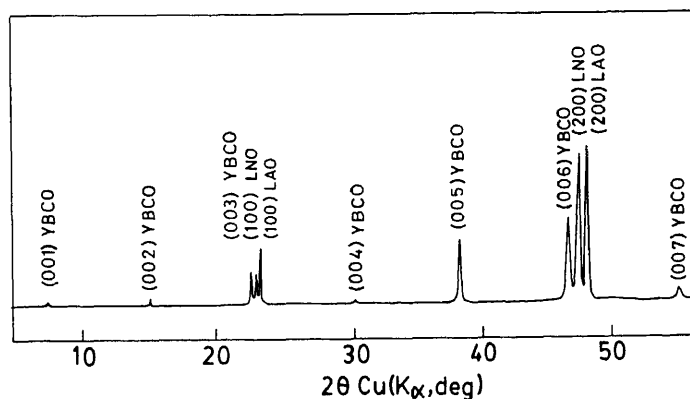


Figure 5. $\text{CuK}\alpha$ X-ray θ - 2θ scan of LaNiO_3 (LNO) films grown on $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) films deposited on LaAlO_3 (LAO) substrate.

4.3 LaNiO_3 as a normal metal barrier for SNS junction

YBCO/LNO/YBCO trilayer structures were fabricated in the planar form with LNO barrier thickness of the order of $1000 \text{ \AA}$. The CuK_α X-ray θ - 2θ scan of YBCO/LNO/YBCO/STO trilayer structure is similar to that given in figure 5. This indicates that the third (YBCO) layer grown LNO is also c -axis-oriented.

In order to measure the I - V characteristics of the above structure, a $100 \mu\text{m}$ wide and $330 \mu\text{m}$ long microbridge was patterned by laser irradiation. Figure 6 shows the I - V characters of the junction at 77 K . The T_c of the YBCO film across the LNO barrier was about 86 K and J_c of the junction at 77 K was 300 A/cm^2 . The coherence length ζ_n in the normal metal (LNO) region was found to be $125 \text{ \AA}$, which was calculated using the formula

$$J_c(d) = J_{c0} \exp(-d/\zeta_n),$$

where d is the barrier thickness.

The figure of merit of the Josephson junction $R_n A$ is found of the order of $10^{-9} \Omega \cdot \text{cm}^2$, which is comparable to the values reported for SNS junctions fabricated using YBCO superconducting films with different metallic-oxide films as barrier layers (Char *et al* 1993).

4.4 LaNiO_3 films as electrodes for ferroelectric oxides

The main problem of integrating ferroelectric thin films into devices is the difficulty of growing single-crystal-like films with proper electrode materials. Recent developments in oxide thin film fabrication reveal that perovskite-related metallic oxides can act as good electrodes for ferroelectric oxides (Ramesh *et al* 1991). Since we have already

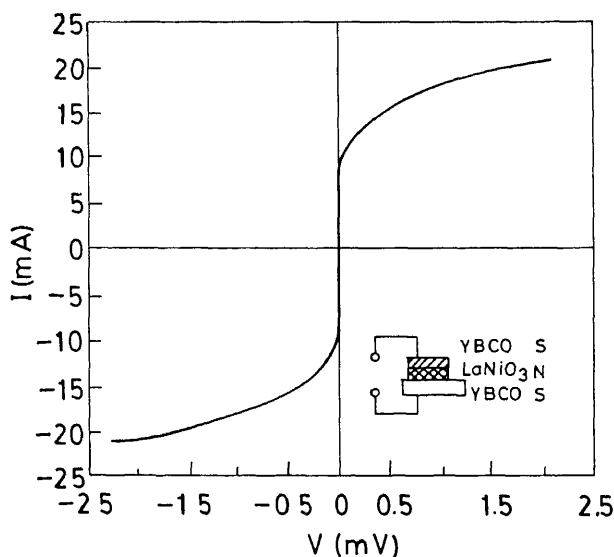


Figure 6. I - V characteristics of YBCO/LNO/YBCO junction.

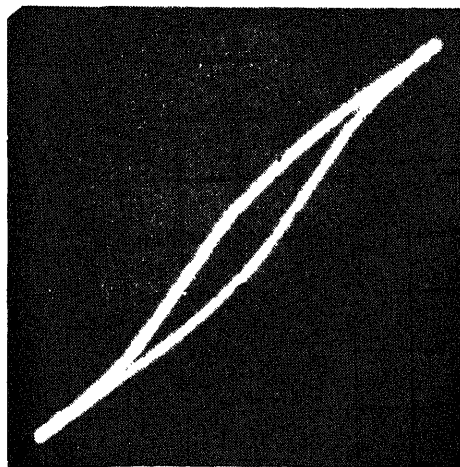


Figure 7. Hysteresis loop of ferroelectric $\text{Bi}_2\text{VO}_{5.5}$ film in the $\text{LaNiO}_3/\text{Bi}_2\text{VO}_{5.5}/\text{LaNiO}_3/\text{SiO}_2/\text{Si}$ trilayer configuration.

developed processes for LaNiO_3 films, we considered it worthwhile to explore this material as an electrode for $\text{Bi}_2\text{VO}_{5.5}$ ferroelectric oxide (Prasad *et al* 1993).

$\text{Bi}_2\text{VO}_{5.5}$ thin films were grown on $\text{LaNiO}_3/\text{SrTiO}_3(100)$ as well as $\text{LaNiO}_3/\text{SiO}_2/\text{Si}$. LaNiO_3 metallic film here acted as the bottom electrode. Experiments were carried out with both Au as well as LaNiO_3 as the top electrode. The trilayer $\text{LaNiO}_3/\text{Bi}_2\text{VO}_{5.5}/\text{LaNiO}_3$ film with the LaNiO_3 electrodes indeed showed the ferroelectric hysteresis loop shown in figure 7. Such a loop could be obtained with just 5 V across the ferroelectric oxide layer. The remanent polarization (P_r) is of the order of 10^{-7} C/cm^2 . This clearly demonstrates the utility of LaNiO_3 as an electrode material. Characteristic ferroelectric property in the form of the hysteresis loop seen here further suggests the growth of stoichiometric $\text{Bi}_2\text{VO}_{5.5}$ thin film. It has also been shown that the trilayer growth is indeed epitaxial (Hegde, unpublished).

4.5 Giant magnetoresistance in $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ thin films

Giant magnetoresistance (GMR) effect was first observed in $(\text{Fe/Cr})_n$ multilayer thin films. Here, large negative resistance is observed when magnetic field is applied and such an effect is likely to be useful for magnetoresistive 'read' heads in information storage devices. Lanthanum manganates doped with Ca, Sr, Ba and Pb are known to show ferromagnetic ordering at temperatures below 320 K and $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$ thin films did show over 50% GMR (Von Helmolt *et al* 1993). We considered it worthwhile to pursue this aspect and here we report GMR in $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ thin films.

The films of $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ were prepared by PLD with almost similar conditions as the LaNiO_3 films. In figure 8, we show the $\Delta R/R_0$ vs H of $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ thin films. Thus for the first time we show here that over 40% GMR is seen in $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ thin films at room temperature. Details of this experiment are published elsewhere (Sundar Manoharan *et al* 1994).

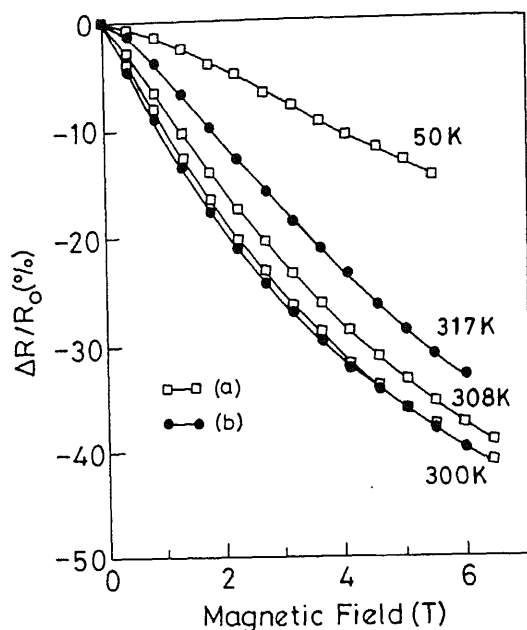


Figure 8. Giant magnetoresistance $\Delta R/R_0$ vs magnetic field for ferromagnetic films of (a) as-deposited epitaxial $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ and (b) partially oxygen-desorbed $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$.

5. Conclusions

We have presented in this article fabrication of epitaxial thin films of Ag-doped YBCO on sapphire, LaNiO_3 metallic oxide, ferroelectric oxide and ferromagnetic $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ oxide by pulsed laser deposition and some of their properties. The results presented here indicate that PLD is a versatile technique to fabricate a variety of oxide thin films for various applications. We expect to bring out some practical devices such as microwave transmitters, SQUIDS, ferroelectric switches and ferromagnetic switches out of these oxide thin films.

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Surfactants: materials for interface design and spontaneous formation of structures

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Abstract. This paper mostly describes the research on surfactant solutions performed at this centre in the past few years. A correlation between microemulsion structure and precipitation reaction of AgCl is described. Experimental and theoretical research culminating in the development of a theme for analysing the structure of colloidal systems is described. Recent results on the discovery of new viscoelastic surfactant systems are presented.

Keywords. Surfactants; cloud point; mixed micelles; viscoelasticity; microemulsions.

1. Introduction

Surfactants are molecules with one end hydrophobic and the other hydrophilic (Shah 1977). Because of this they accumulate at interfaces reducing the interfacial tension and also forming various spontaneous structures like monolayers, micelles and microemulsions in water and/or hydrocarbon media (Corti and Degiorgio 1980). These systems resemble structures like the cell membranes of biological systems and hence are of great interest. This article is restricted to three aspects to which we have made contributions, namely microemulsions, clouding phenomenon, and viscoelastic surfactants.

2. Microemulsions

Microemulsions are thermodynamically stable, isotropic, transparent mixtures of water, oil and suitably chosen surfactants. Therefore the microemulsion is neither an aqueous nor a nonaqueous liquid which has microstructures on the scale of ~ 100 Å. This system has emerged as a curiosity for physics of novel structures and for chemistry in confined geometries. They have wide-ranging and novel applications which range from self-extinguishable fuel for defence applications to pesticide concentrate formulation in agriculture. They are ideal systems for studying the relation between structure and chemistry.

Figure 1 shows data from some of the studies carried out on the microemulsion of benzene/water/SDS/isopropanol (Leung *et al* 1985). Two aspects, one structural and the other chemical reactions, were investigated primarily with the idea of understanding the interrelation between the structure and reaction rates. The reaction studied was the precipitation of AgCl in microemulsion. Two identical microemulsions were prepared, one with AgNO₃ and the other with NaCl. These two were mixed in a stop-flow apparatus and the development of turbidity due to precipitation was monitored with time. It was interesting to see that the rate at which the transmittance decreased due to precipitation was dependent on the structure of the medium. The changes in the structure were also reflected in studies of conductivity, ultrasonic

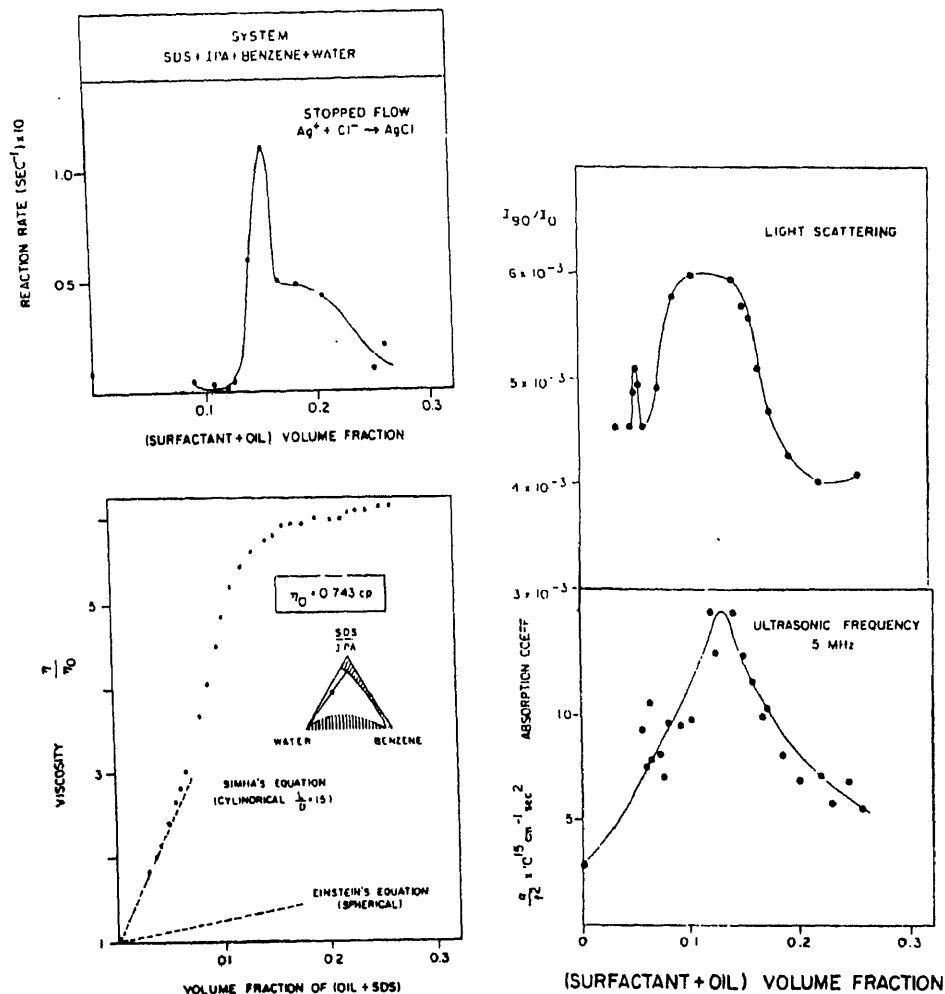


Figure 1. Data for a microemulsion with the components shown and with weight ratio of SDS/IPA = 0.5 investigated with several techniques show that around volume fraction of OIL + SDS = 0.15 some structural change occurs which seems to affect the precipitation rates of AgCl.

absorption, etc (figure 1). These studies conclusively showed the relation between chemical reactions and structure in these systems. In recent years these studies have emerged as a way of preparing nanophase materials of a variety of compounds.

3. Clouding phenomenon

Nonionic surfactant solutions in water at a level of about 1% by weight undergo a phase separation into a surfactant-rich phase and a water-rich phase on heating. Associated with this transition is an intense scattering of light as one approaches the phase-separation temperature, the cloud point. This quantity plays an important role in detergency and the mechanism poses an interesting challenge to physicists and

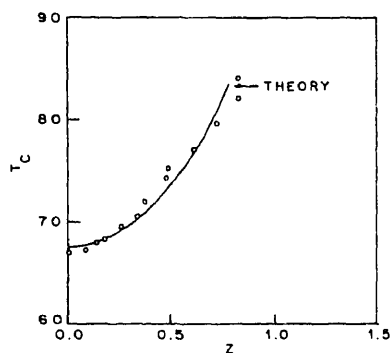


Figure 2. Cloud point measurements of Triton X-100 + SDS shown as the charge on the micelle is varied. The quadratic fit gives the micellar diameter (Manohar and Kelkar 1990) and confirms that the clouding phenomenon is due to interaction between micelles.

chemists. There have been two points of view to understand this phenomenon. One suggests that the surfactant which is water-soluble at room temperature becomes insoluble at higher temperature due to the breaking of hydrogen bonds between the surfactant and water (Mukherjee 1972). The other school suggests that there is an enhanced attraction between the micelles at higher temperatures resulting in a phase separation between micellar phase and water (Corti and Degiorgio 1980). We argued that if the latter is true then any change in the nature of interaction between the micelles should be reflected in a change of the cloud point. We increased the repulsion between micelles of the uncharged surfactant Triton X-100 by incorporating a charged surfactant sodium dodecyl sulphate (SDS) in a controlled way. The cloud point increased, indicating that the interaction between the micelles was important in clouding (Valaulikar and Manohar 1985). Several groups have followed this 'trick' and have come to the same conclusion (Marszall 1988; Gu *et al* 1989; Huang and Gu 1990). We developed a semiquantitative model to interpret the rise in cloud point and to obtain micellar diameter from these measurements (Manohar and Kelkar 1990). These results are shown in figure 2. Meanwhile our colleagues at BARC had developed the small angle neutron scattering (SANS) technique and this turned out to be the most suitable for investigating the structure of micellar systems (Desa *et al* 1985; Goyal *et al* 1988, 1989). The results obtained for the structure of these systems required not just the semiquantitative models but a more rigorous treatment of the interactions between the micelles. The literature showed that there did not exist suitable theories which take into account the attractive interactions accurately. The most popular model was that by Hayter and Penfold (1981) and this was more suitable for systems where Coulomb interactions dominated. We thought that the more appropriate liquid-state theory for attractive interactions was that of Baxter and adopted it for micellar systems with quantitative description of the SANS data in the literature (Menon *et al* 1991a). The model was put on a more rigorous footing by realizing that the Baxter model can be looked upon as a perturbation expansion in powers of Δ/σ , where Δ is the range of attractive interactions and σ the diameter of the micelle (Menon *et al* 1991b). Since for colloidal systems this ratio was smaller than unity the Baxter model appeared to be the most natural one to use for colloidal systems. The structure factors calculated using our approach and comparison with

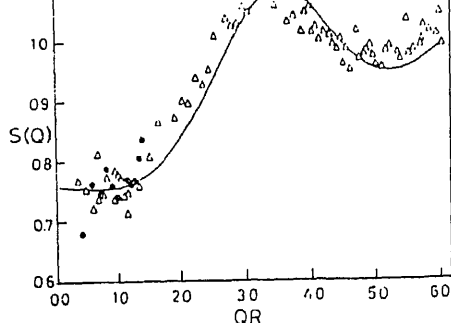


Figure 3. The structure factor calculated (line) by Baxter model without any adjustable parameters (Menon *et al* 1991) compared with Monte Carlo calculations (circles and triangles) of Huang *et al* (1984). This case is appropriate for a micellar system.

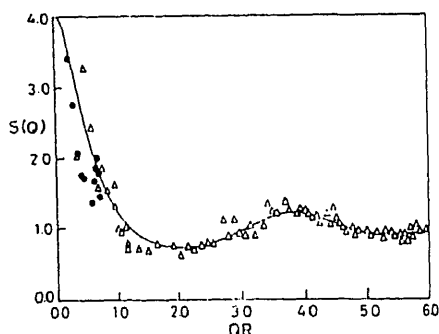


Figure 4. Structure factor similar to figure 3 but this case is more appropriate to a microemulsion.

the Monte Carlo simulations are shown in figures 3 and 4. Once this was realized the need to extend the Baxter model to include the Coulomb interactions became necessary because the majority of the systems in nature are charged systems. We used the Baxter model as the zeroth-order solution to the Ornstein–Zernicke equations and treated the Coulomb interaction in the random phase approximation (Manohar and Kelkar 1992; Kelkar *et al* 1992). Fortunately, just at that time some French scientists had discovered an ionic surfactant which showed clouding and they had failed to describe their SANS experiments by the existing theories of Hayter and Penfold (Warr *et al* 1990). It turned out that our Baxter–RPA model was able to fit these data quantitatively with ease (Manohar and Kelkar 1992). Meanwhile experiments on SANS and cloud point measurements had been initiated on two systems, namely a mixture of sodium salicylate (SS) + Triton X-100 and SDS + Triton X-100. The former system, in particular, was extremely neat because one could combine the chemistry and physics beautifully to tune the intermicellar interactions just by tuning the pH of the system (Manohar *et al* 1990) and the system was amenable for quantitative interpretation with minimum parameters. The cloud point

measurements and the fits to results of calculations are shown in figure 5. The model turned out to be good for this situation. The second system of SDS + Triton X-100 too was found to be quantitatively describable by the Baxter-RPA model we had put forward (Kelkar *et al* 1991). In this system we also observed the phenomenon of

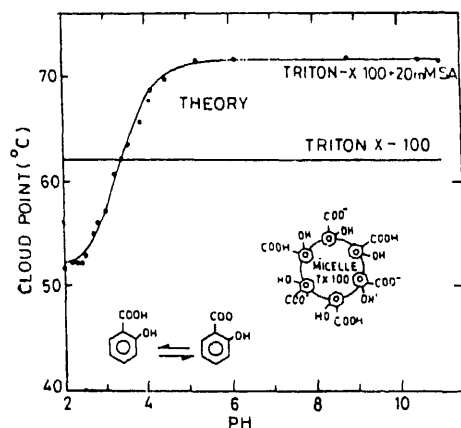


Figure 5. Cloud point altered by tuning the relative strengths of van der Waals and Coulomb interactions by changing the pH of the system, and the equations calculated using the interaction between the micelles (Manohar *et al* 1990): a beautiful combination of chemistry and physics.

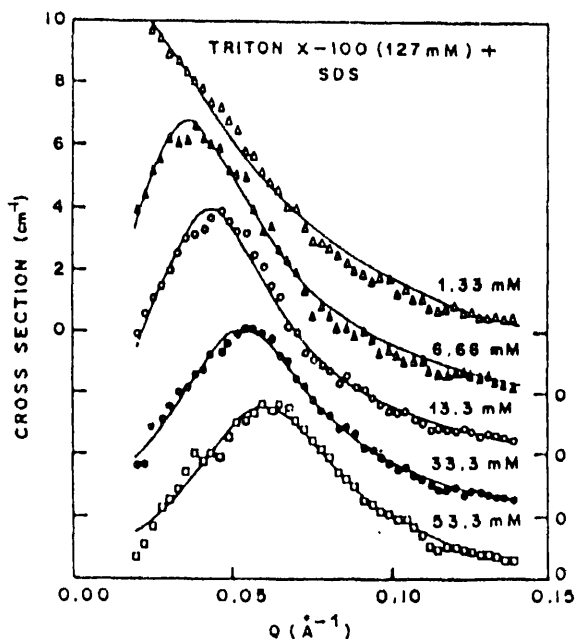


Figure 6. SANS results on Triton X-100 (127 mM) + SDS, concentrations shown, and Baxter-RPA model (Manohar and Kelkar 1992) calculations denoted by lines (Kelkar *et al* 1991).

charge condensation on micellar surface. The experimental results of SANS and the result of calculations of RPA-Baxter model are shown in figure 6. On the whole the investigations on the clouding phenomenon turned out to be exciting with the emergence of a theme for description of colloidal systems.

4. Viscoelasticity

Cationic surfactants like cetyltrimethylammonium bromide (CTAB) show the interesting phenomenon of drastic increase in viscosity and even elasticity on addition of additives like SS. Such systems have been of great interest and have been investigated in the literature. These are called by various names, e.g. worm-like micelles, thread-like micelles, living polymers. Some aspects of these systems have not been understood, namely the following:

(i) The rise in viscosity shows specificity. If one shifts the OH group in SS to *meta* or *para* position the viscoelastic effects decrease drastically (Manohar *et al* 1986).

(ii) When one adds additives like SS to CTAB the viscosity shows two peaks as the

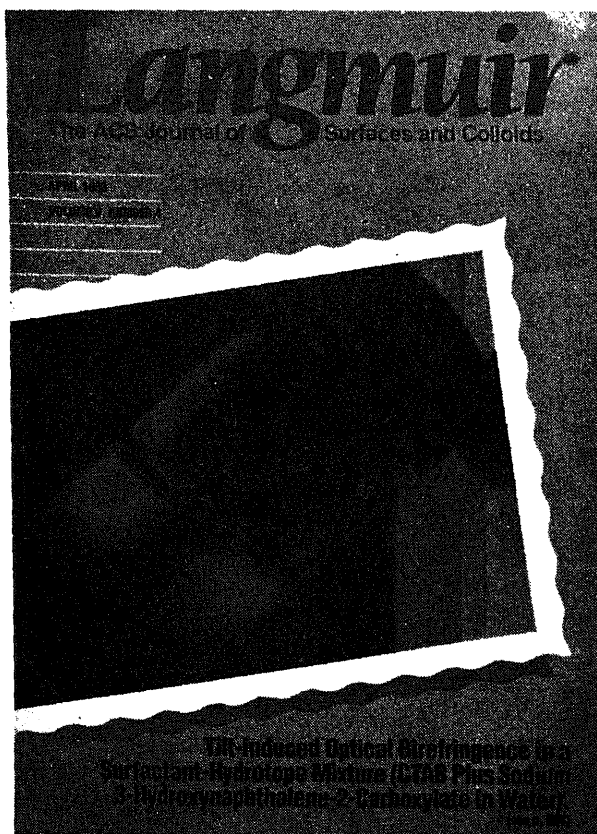


Figure 7. A strongly viscoelastic solution of CTAB and SHNC is observed to show tilt-induced birefringence (Mishra *et al* 1993).

concentration of SS is increased keeping the amount of CTAB constant (Rehage and Hoffmann 1991).

(iii) In between the two peaks in the viscosity one observes in some systems phase separations and liquid crystalline phases (Rehage and Hoffmann 1991; Mishra *et al* 1993).

With a view to understanding the specificity effects we performed NMR experiments on CTAB-SS systems and observed an interesting aspect in the SS part of the NMR spectrum. The SS molecules were adsorbed on micellar surface with their carboxylic groups sticking out in water (Rao *et al* 1981; Manohar *et al* 1986). This implied that the SS molecule was surface active! In the literature it had not been recognized that molecules like SS could be surface active. This was further confirmed by other workers in India (Balasubramanian *et al* 1989). Once this feature was realized we were able to design new systems which were viscoelastic and one with sodium hydroxynaphthalene carboxylate (SHNC) proved to be most exciting (Sushama Mishra *et al* 1993; Manohar and Janaky Narayanan 1994). This was strongly flow birefringent and just a small tilt in the sample induced the birefringence (figure 7). In this system we observed the nematic phase, which provided the first link between nematics and viscoelastic systems. This aspect is most interesting because nematic liquid-crystalline polymers have been known and it is most likely that the ideas from this field become translatable to surfactant solutions. We are investigating these systems and expecting to derive a lot of excitement in the coming years.

In summary, the developments mentioned above have led not only to just a set of disjointed papers but what has emerged is a theme and, more importantly, a group of scientists interested in surfactants and recognized in international circles.

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polymer structure effect on gas permeation characteristics in polyarylates

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Abstract. This paper reviews recent investigations of the factors which control gas transport in a series of highly aromatic polyarylates. The polymer physical properties which correlate with its intrinsic separation characteristics were elucidated by studying well-defined families of polyarylates. Molecular modelling was used to understand the effects of various substitutions in the polymer structure and the mechanism through which the polymer properties are affected. The effect of polymer chain mobility, conformation and packing density on the permeation characteristics are discussed.

Keywords. Permeation; polyarylates; gas separation.

Introduction

Polymers which are used to fabricate gas separation membranes need to meet several criteria such as high permeability to the desired gas, high selectivity, ability to be formed into useful membrane configurations, and resistance to processing conditions of high pressure, moisture, etc. The most important criteria are the polymer permeation characteristics. The economic viability of membrane gas separation depends greatly on membrane productivity, i.e. flux per unit membrane surface area. This is a function of both the intrinsic permeability of the membrane material and the ability to form it into a thin, defect-free film. The permselectivity of the membrane material establishes the maximum separation achievable.

The ideal membrane material would combine high permeability with high permselectivity. Unfortunately, polymers in general show an inverse correlation between these two properties. Polymers with high permeabilities tend to have low selectivities, and vice versa. Identification of new materials which overcome this natural trend is required for improving the cost effectiveness of membrane gas separations.

Recently, systematic studies of polymer structure-permeability relationships in several families of glassy polymers have led to the identification of new materials for gas-selective membranes which combine high permeability and permselectivity. Such studies have been carried out for polyimides (Kim *et al* 1988; Stern *et al* 1989; Coleman and Koros 1990), polycarbonates (Anand *et al* 1989; Schmidhauser and Longley 1990), polysulphones (McHattie *et al* 1991; Houde *et al* 1994) and polyarylates (Sheu and Chern 1989; Charati *et al* 1991a). Polyarylates in particular are a promising class of membrane materials particularly for air separation. The potential of using polyarylates as a membrane material can be seen in the study (Barbari *et al* 1989) of four types of polymers based on bisphenol-A (Bis-A), viz. polyarylate, polycarbonate, polysulphone and polyetherimide. The gas permeability of the polyarylate based on bisphenol A and equimolar mixtures of isophthalic and terephthalic acids was higher than in the other polymers.

1.1 *Polymer characteristics which influence transport properties*

It would be desirable to understand the effect of various polymer characteristics on permeability. Transport properties of gases are known to depend on structural parameters like packing density in the polymer, polar group density, chain rigidity, and molecular mobility (as determined by glass, T_g , or lower transition, T_v , temperatures). Establishing polymer structure-permeability correlations is important for rational design of new polymers for specific gas-separation applications. This paper reviews some of our recent work with polyarylates towards this goal.

Recent work has identified several polymer characteristics which as a general rule are found to affect either the permeability or the permselectivity. The effect of decreasing packing density of the polymer matrix on increasing diffusivity and permeability has been shown in several types of polymers (Kim *et al* 1988; Stern *et al* 1989; Charati *et al* 1991a). It has also been shown that simultaneous inhibition of the interchain packing and restriction of the intrasegmental mobility as a result of substitution by a bulky group results in a polymer structure which leads to high permeability and selectivity (Hoehn and Richter 1980; Kim *et al* 1988). The opposing effects of polymer polarity (increased interchain packing coupled with increased gas-polymer interaction) on gas permeability have been reported (Muruganandam *et al* 1987). Other parameters investigated include the dielectric constant (Matsumoto *et al* 1993) and charge transfer complex formation (Stern *et al* 1989).

1.2 *Rational design of polymer structure*

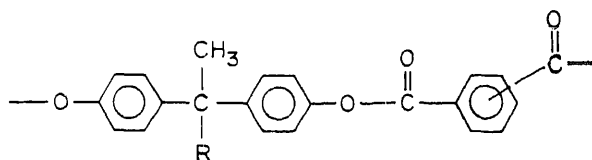
While definitive a priori design of a polymer with specified permeation characteristics is not yet possible, much progress has been made towards this goal. As mentioned above, there are now consistent data correlating various polymer characteristics with permeation properties. However, it is still difficult to relate these properties to the chemical repeat-unit structure of the polymer. Empirical correlations exist where group additivity methods have been used for correlating polymer permeabilities. Such correlations (e.g. the well-known 'permachor' method proposed by Salame 1967) are useful for describing variation over several magnitudes of permeability values; however, these do not give the fine insight required for deciding how to modify a given polymer. Semi-empirical models exist which relate polymer characteristics to transport phenomena. Such models based either on activation-energy concepts (Pace and Datyner 1979) or on free-volume models (Kulkarni and Stern 1983) can be used to predict diffusivities if some polymer physical characteristics are known. However, these models do not have a direct relationship with polymer structure.

2. **Present approach**

To increase our understanding of the effect of polymer structure on permeation properties, the four-step approach followed by us is given below:

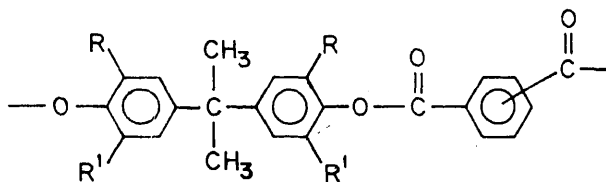
A. Systematic synthesis. Families of polyarylates with systematic variations in the chemical structure have been synthesized. In the case of polyarylates which are prepared by the condensation reaction of aromatic diols and acids, it is possible to

modify either reactant. The modified polymers can then be compared with the base material. Starting with the polyarylate formed from bis-A and equimolar mixtures of terephthalic and isophthalic acids as the base material, two families of new polyarylates synthesized with systematic modifications of the bisphenol are shown in figures 1 and 2 (Charati *et al* 1991a). In figure 1, one methyl group at the bridge carbon atom is changed to either a longer flexible alkyl group (ethyl), a branched alkyl group (isobutyl), an aromatic group (phenyl), or a polar alkyl group (methyl propionate). In figure 2, the bisphenol phenyl rings are substituted with either nonpolar (methyl) or polar ($-\text{Br}$) groups. This substitution pattern may be either symmetric (tetramethyl) or asymmetric (dimethyl).



- i) $R = -\text{CH}_3$ (PBis-A)
- ii) $R = -\text{CH}_2-\text{CH}_3$ (PBis-MEK)
- iii) $R = -\text{CH}_2-\text{CH}(\text{CH}_3)_2$ (PBis-MIBK)
- iv) $R = -\text{C}_6\text{H}_5$ (PBis-Aceto)
- v) $R = -\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{CH}_3$ (PBis Lev)

Figure 1. Structure of bisphenol bridge carbon mono-substituted polyarylates.



- i) $R = R' = -\text{CH}_3$ (PTMBis-A)
- ii) $R = -\text{H}, R' = -\text{CH}_3$ (PDMBis-A)
- iii) $R = R' = -\text{Br}$ (PTBr Bis-A)

Figure 2. Structure of bisphenol phenyl ring substituted polyarylates.

B. *Polymer characterization.* The synthesized polymers are characterized for various physical properties of interest and these are compared with the permeation properties.

For example, in the first series described above (figure 1), consisting of bridge-substituted polyarylates, the interchain spacing (d -spacing or d_{sp} , measured by WAXD) is kept constant. The $>C=O$ group density and the solubility parameter are also relatively unchanged. In this series the effects of different types of substitutions on the glass transition temperature, T_g , and the γ transition temperature and correspondingly on permeability can be seen. In this manner, the effect of chain rigidity can be examined in isolation from other variables.

In the second series, of ring-substituted polyarylates, the effects of symmetry and polarity of the substituent groups is investigated. These substituents cause varying amounts of changes in all four parameters, viz. the d -spacing, the $>C=O$ group density, and the glass and γ transition temperatures.

C. *Heuristic rules.* Some generalizations can be made relating the physical-property variations with the permeation-property changes in the polymer series. Such rules may be useful if applicable over a wide range of polymers. In the case of polyarylates, it is possible to describe the effects of polymer chain mobility, polarity and packing density on the permeation characteristics.

D. *Molecular modelling.* Molecular modelling can be used to explore the mechanism by which chemical structure affects physical properties in order to gain a more meaningful insight and also to guide future synthesis. Because of their highly glassy, amorphous nature, polyarylates are not easy to characterize. In particular, molecular-level information is difficult to obtain. In such cases, molecular modelling can be used to understand the effects of various substitutions in the polymer structure and the mechanism through which polymer properties are affected.

3. Heuristic rules relating polymer transport properties with other characteristics

Some general rules are discussed below and illustrated with examples from the work with polyarylates.

3.1 Effect of packing density

Modifications in polymer structure which reduce the packing density lead to a decrease in selectivity and increase in permeability. This result is also predicted by both activation-energy and free-volume models of gas transport. The packing density of the polymer can be characterized in two common ways: (i) by wide-angle X-ray diffraction (WAXD), (ii) by density measurements. The WAXD spectra of amorphous polyarylates show a broad peak; the peak maximum is used to calculate an average intersegmental distance, d_{sp} , characteristic of that polymer. Density measurements in combination with group additivity methods to calculate the van der Waals volume of the polymer segment can be used to calculate the free volume of the polymer.

Both the free volume and the d_{sp} are measures of the packing density of the polymer; however Charati *et al* (1991a) have indicated that for several types of highly glassy

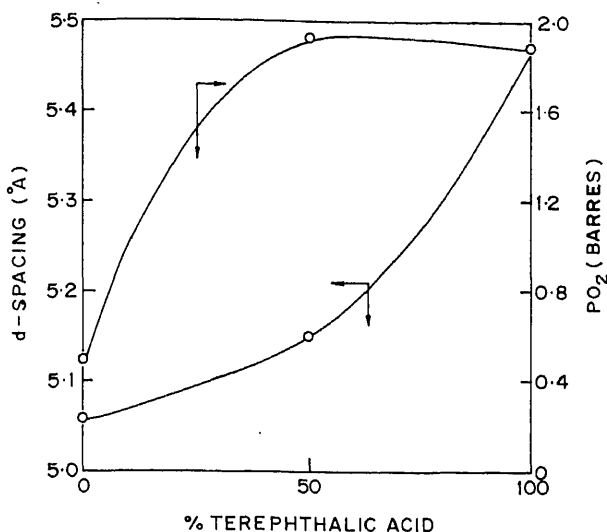


Figure 3. O_2 permeability and d -spacing as a function of terephthalic acid content in polyarylates based on bisphenol-A and iso/terephthalic acids.

polymers, the d_{sp} correlates better with the permeability than the free volume. The difference may arise because of errors in calculating the van der Waals volume by the group additivity method.

An example of a correlation between d_{sp} and permeability is shown in figure 3. Most polyarylates made with isophthalic and terephthalic acids show increasing d_{sp} values as the proportion of terephthalic acid is increased; there is a corresponding increase in permeability. Similar correlations can be found for polyimides (Coleman and Koros 1990).

A general trend is that permselectivity decreases with increasing d_{sp} ; this is to be expected as a more open polymer matrix will have less ability to discriminate between penetrants on a steric basis. A more subtle effect may also be useful: the increase in permeability of various gases appears not to be uniform with increasing d_{sp} values. In some ranges of d_{sp} values, the free-volume distribution may change so as to allow a larger increase in permeability of smaller penetrants, e.g. He, while the permeability of larger molecules, e.g. N_2 , may increase by a smaller amount, thus resulting in a selectivity increase for smaller molecules. This result is the reverse of the predictions from either activation-energy or free-volume models in which the increase in permeability with decreasing packing density would be more for larger molecules. However, neither of these theories account for the concept of free-volume distribution.

The d_{sp} can also be used to characterize the increase in permeability on plasticization of the polymer from exposure to high-pressure gases with high solubility, e.g. CO_2 . The change in permeability profiles with increasing pressure can be related to the increase in d_{sp} for several classes of polymers (Houde *et al* 1992).

2. Effect of chain rigidity

The chain rigidity is characterized by the glass transition temperature T_g or lower transition temperature T_v , measured using dynamic mechanical analysis (DMA) or

Table 1. Physical properties and O₂ permeability of bridge-substituted polyarylates.

Bisphenol	<i>d</i> -spacing (Å)	Solubility parameter (δ)	Transition temperatures		Permeability (Barrers) O ₂
			<i>T_g</i> (°C)	<i>T_y</i> (°C)	
Bis-A	5.15	9.91	198	-84	1.4
Bis-MEK	5.18	10.01	192	-92	1.6
Bis-MIBK	5.21	9.56	216	-72	3.5
Bis-Aceto	5.09	9.94	267	-85	2.1
Bis-Lev	5.03	10.22	165	-93	0.76

All bisphenols polymerized with equimolar mixture of isophthalic and terephthalic acids.

Structure of bisphenols used above as in figure 1

Bis-A : R = R' = -H

Bis-MEK : R = -CH₃, R' = -CH₂-CH₃;

Bis-MIBK : R = -CH₃, R' = -CH₂-CH(CH₃)₂;

Bis-Aceto : R = -CH₃, R' = phenyl;

Bis-Lev : R = -CH₃, R' = -CH₂-CH₂-COOCH₃;

Permeation study at 35°C and at 1×10^6 N/m².

differential scanning calorimetry. Analysis of a systematically varied family of polymers by DMA in particular gives much useful information regarding polymer chain mobility (Charati *et al* 1994).

Previous studies on the effect of chain rigidity as measured by these transition temperatures (*T_y* or *T_g*) have indicated that increasing chain rigidity correlates with reduced permeability (e.g. Light and Seymour 1982). This is generally accepted to be the case for rubbery polymers; however the situation is not so clear for highly glassy polymers. In previous studies the packing density was not kept constant and hence this conclusion may have been premature. Recent work (Houde *et al* 1995) indicates that in a family of bridge-substituted bisphenol-A-based polyarylates (figure 1), the *d_{sp}* is relatively constant and the permeability increases as *T_y* increases (see table 1). More work will be necessary to validate this finding.

3.3 Simultaneous increase in chain rigidity and decrease in packing density

Kim *et al* (1988) have shown the utility of this rule, first developed by Hoehn and Richter (1980), for a series of polyimides. Modifications in polymer structure which lead simultaneously to an increase in chain rigidity and also a decrease in packing density result in an increase in permeability without loss of selectivity. This rule applies equally well to polyarylates and polysulphones (Houde *et al* 1994).

An example of this rule can be seen by comparing the polyarylates prepared from bisphenol-A and then modified by the tetramethyl substitution (see table 2). The Me₄Bis-A polyarylate is more rigid (higher transition temperatures) and has lower packing density (higher *d_{sp}*). Correspondingly, its permeability is increased three-fold without hindering permselectivity.

Table 2. Physical properties and permeation characteristics of ring-substituted polyarylates.

Bisphenol	<i>d</i> -spacing (Å)	<i>T_g</i> (°C)	Permeability	Selectivity (He/CH ₄)
			(Barrers) He	
Bis-A	5.15	198	16	40
DMBis-A	5.21	235	13.6	170
Me ₄ Bis-A	5.74	274	47	65
Br ₄ Bis-A	4.15	285	14.1	83

All bisphenols polymerized with equimolar mixture of isophthalic and terephthalic acids.

Structure of bisphenols used above as in figure 2

Bis-A : R = R' = -H

Me₄Bis-A : R = R' = -CH₃

Br₄Bis-A : R = R' = -Br

Permeation study at 35°C and at 1×10^6 N/m².

Effect of polarity

Increased solute-polymer interaction would tend to increase solubility of the solute and thereby increase its permeability (e.g. see Chern *et al* 1987). Increase in permeability through increasing the polar-group proportion in a polymer would be expected to be particularly effective in the case of gases like CO₂ or O₂ relative to H₂ or inert gases.

The effect of polarity may be double-edged in that it may also lead to increased polymer interchain interactions causing a decrease in permeability. This can be seen by comparing the tetrabromo and tetramethyl substitutions on the bisphenol-A phenyl rings (table 2).

Insights from molecular modelling

While molecular modelling cannot be used yet to a priori design polymers for gas separation, it can be used to rationalize and understand the experimental results. As a result of these insights, it can suggest further polymers for synthesis.

The calculations used for obtaining the results described here are done with a conventional software package (CharmM) based on molecular-mechanics approximations. An electron delocalization term was added separately to the energy calculations (Harati *et al* 1991b).

Polyarylate isomers

Intuitively, it would appear that polyarylates made with terephthalic acid would be more linear and pack denser than the corresponding polyarylates made with isophthalic acid. Actually, as indicated earlier (figure 3), the reverse is true and in general the terephthalic acid-based polymers have higher *d_{sp}* and permeability values.

Modelling shows that the results are reasonable in terms of their three-dimensional structure. While the isophthalic acid and bisphenol-A-based polyarylate has a regular helical structure, the one based on terephthalic acid has a crank-shaft-type configuration. Packing of individual chains into assemblies shows that the isophthalic acid-based polymer chains have a 20% smaller interchain separation than the terephthalic acid-based polymer (Vetrivel *et al* 1991). This is the explanation for the data shown in figure 3.

4.2 Bridge-substituted polyarylates

The bridge-carbon-substituted bisphenol-A and isophthalic/terephthalic acid-based polyarylates have relatively constant d_{sp} values irrespective of the fact that the methyl group is substituted by more bulky groups. Normally, one would expect bulky groups to alter the chain conformation or prevent chains from approaching each other and lead to lower packing density. In this case, in the preferred (energy-minimized) chain conformation, the mono-substituted group is oriented towards the outside of the helix. The chain conformation is not altered significantly and this prevents the d_{sp} from changing much (see table 1).

4.3 Phenyl-ring substituted polyarylates

Energy mapping of the rotational mobility of various dihedral angles in the polymer chain has indicated the importance of the bisphenol phenyl rings in governing the overall chain rigidity (Charati *et al* 1991b). The rotational mobility of the phenyl rings is important for determining the calculated configurational entropy which correlates well with the observed T_g . The phenyl ring mobility has also been related to the γ transition in both polyarylates (Charati *et al* 1994) and polycarbonates (Yee and Smith 1981). The ortho hydrogen repulsion on adjacent phenyl rings is an important variable determining chain conformation. These observations from the molecular modelling work provide a rationalization of the large change in chain rigidity and interchain spacing, and consequently permeability as a result of phenyl ring substitution (table 2).

Results (to be published) indicate that in polyarylates with such substitutions the interchain separation is dominated by the tetra-substituted bisphenol moiety and the effect of the acid group (isophthalic or terephthalic) in determining d_{sp} is wiped out. The reason for this is the change in chain conformation and decrease in chain colinearity necessitated by accommodating the phenyl ring substituents.

In the case of asymmetrically substituted phenyl rings (dimethylBis-A) the d_{sp} does not change dramatically; however, the free-volume distribution may be shifted towards lower values. DMBis-A-based polyarylates appear to give higher selectivities than other polyarylates (see table 2). In order to get both high selectivity and high permeability, polymers can be designed with an asymmetrically substituted bisphenol-A to give selectivity and a modified acid which promotes high permeability. A novel polymer based on this principle has recently been synthesized and shown to have an O_2 permeability of 1.5 barrers and O_2/N_2 selectivity of 8–9 (Jadhav *et al* 1993).

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Biomaterials: Role of surface modifications

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Abstract. The fundamental concepts related to biomaterials and blood/tissue–material interactions at the interface have been reviewed. The relevance of surface modification to enhance blood and/or tissue compatibility of materials has been discussed and its role in selected prosthetic applications described.

Keywords. Biomaterial; surface modification; protein adsorption; blood compatibility; tissue compatibility; calcification; hemoperfusion; artificial skin.

1. Introduction

When one looks at the intima of a blood vessel, it appears hydrated, gelatinous, flexible and multiphase to prevent protein and platelet reactions with its carbohydrate-rich outer coat (Rigby 1961). Further, on closer investigation, one will find a definite arrangement of endothelial cells having specific physiological responses, even secreting pharmacologically active substances such as prostaglandin PGI_2 possessing antiplatelet activity by stimulating membrane-bound adenylyl cyclase and thereby raising the intracellular levels of cyclic AMP (cAMP) within platelets (Moncada and Vane 1979; Bonne *et al* 1981). Thus the intima's complex role of keeping the blood flowing in living blood vessels makes it impossible to duplicate it by any artificial means. Attempts have been made by grafting hydrogels, developing textures or microdomain structures, or hydrophobic–hydrophilic optimization on polyurethane substrates (Sharma 1991) to enhance blood compatibility. Negative surface charge (Sawyer 1985) and even electrical conduction and semiconduction properties based on specific structural regularity of various proteins and polymers also seem to play a role in enhancing blood compatibility (Bruck 1979).

Scientific efforts have been made to immobilize covalently (or facilitate controlled release of) the selected bioactive molecules such as PGI_2 , PGE_1 , phosphorylcholine, heparin, hirudin, urokinase or streptokinase, antithrombin III, cAMP collagen, etc and their complexes with albumin onto the substrates along with oral antiplatelet drugs like aspirin; vitamins C, E, B_6 ; antibiotics; etc (Sharma 1991). It seems that antiplatelet biomolecules preferentially promote albumin adsorption. Efforts have also been made to graft heparinoid polyelectrolyte, synthesized in our laboratory from natural rubber on polyetherurethane urea (PEUU) surfaces. These surfaces have a marked effect in decreasing platelet adhesion with minimal protein interaction, and can act as a passive layer enhancing blood compatibility (Sharma and Nair 1984). It has also been found that surfaces adsorbing more high-density lipoprotein (HDL) compared to low-density lipoprotein (LDL) are relatively more blood-compatible (Chandy and Sharma 1991). Endothelialization of porous substrates via cell culture technique with coimmobilization of cell-growth and cell-adhesive factors has also been tried (Ito 1992). However, the problem of immune response and steady supply of cells is not fully solved. Genetically engineered endothelial cells have been

seeded on fibronectin-coated vascular grafts to secrete increased amounts of tissue plasminogen activator enhancing thromboresistance. The production of plasminogen activator has been found to be higher on collagen-impregnated Dacron than on expanded poly(tetrafluoroethylene) (PTFE) or polyurethane/Dacron composite (Shayani *et al* 1992). Pentapeptides have been used to form an elastic matrix via crosslinking by gamma irradiation and addition of fibronectin for cell attachment. Fibroblasts, endothelial cells and other cells have been used for such studies (Urry *et al* 1992). Even a composite graft made of polyurethane-coated pericardium has been developed (Tolia and Sharma 1986), with all these efforts there is still no small-diameter vascular graft (< 5 mm diameter) available today except sephanous vein to replace coronary artery without thrombus formation. Attempts have been made to develop small-diameter vessels from PEUU. However, in *in vivo* trials in mongrel dogs at iliac artery, the graft showed thrombus formation initiated from the suture site at the anastomosis within 20 days (Sharma 1983). Therefore the core of our discussion here is related to the surface energy parameters and the necessity of optimizing them with biophysicochemical aspects comprehensively for understanding the blood/tissue-material interactions at the interface.

2. Background

Any nonliving materials used in a medical device intended to interact with biological systems is called a biomaterial (Williams 1987). Obviously it should be nontoxic, fabricable, sterilizable, and stable during implantation and as required by application. It should not corrode, degrade, or be carcinogenic. Further the ability of a material to perform with an appropriate host response in a specific application is termed biocompatibility. This is controlled at tissue-material interfaces by pore size and density (soft tissue $\approx 50 \mu$, hard tissue (bone) $> 100 \mu$), geometrical nature, controlled chemical breakdown by the resorption of material where material may be replaced by regenerating tissue, and controlled surface reactivity. If the surface reactivity is high, usually healing is delayed by formation of giant cells, and the fibrous tissue layer is much thicker causing tissue instability. Some of the tissue-compatible materials (materials used in contact with tissue) are titanium, cobalt-chromium alloy, bioglass, aluminium oxide, hydroxylapatite, chitosan, etc.

Ideal blood-compatible materials (materials used in contact with blood) do not activate the intrinsic blood coagulation system or to attract or alter platelets or leucocytes (Forbes and Prentice 1978). Blood compatibility of any material is dependent on surface charge, surface free energy, chemical group distribution, heterogeneity, surface texture, porosity, smoothness and flow conditions. International efforts continue towards production of materials that prevent thrombosis, surface modification to enhance blood compatibility, and use of therapeutic substances that prevent deposition of fibrin. Some of the commonly used blood-compatible materials are polydimethylsiloxane, cellulose acetate, polyacrylonitrile, PTFE, nylon, polycarbonate, polyurethane, poly(methyl methacrylate) (PMMA), pyrolytic and low-temperature isotropic (LTI) carbons, etc.

3. Theory and experimental

When any material comes in contact with blood instant adsorption of proteins takes place with a certain selectivity, rate and concentration. The interaction involves

intermolecular forces which develop at the interface, e.g. London dispersion forces, hydrogen bonds, dipole–dipole interactions, donor–acceptor bonds, electrostatic interactions, acid–base interactions, etc. Albumin-coated surfaces do not seem to attract platelets (Lyman *et al* 1968; Kim and Lyman 1973), whereas γ -globulin and fibrinogen coatings cause not only platelet adhesion but also aggregation and release of platelet constituents (Vroman and Adams 1971). The processing parameters also can change the nature of the adsorbed proteins due to variations in microstructure; for example, the glass side and air side of cast polyurethane urea with polypropylene glycol (MW 1025) are found to be different as the air-side domain size is 80–120 Å and the glass-side size 30–50 Å (Sharma 1980).

When blood comes in contact with any material it probably involves the following steps (Vroman 1984–85) in the intrinsic system as follows:

- (i) The factor XII protein (Hageman factor) adsorbed onto the surface becomes activated and this (XIIa) activates other molecules of XII.
- (ii) The molecules of high-molecular-weight kininogen (HMWK) carrying factor XI are adsorbed near factor XIIa, along with other molecules of HMWK carrying prekallikrein.
- (iii) Factor XIIa activates factor XI to factor XIa and converts prekallikrein to kallikrein.
- (iv) Kallikrein can activate more factor XII.
- (v) With the activation of factor XIa the fluid phase of clotting with the requirement of calcium ion begins with further activation of factor IX to IXa.
- (vi) The γ -carboxyglutamic acid groups and the negatively charged groups on the phospholipid droplets with calcium ions as bridges, factor IXa comes closer to factor VIII anchored, in the uncharged group of the phospholipid droplet, factor VIII is converted to VIIIa.
- (vii) Similar reactions progress and convert factor X to Xa, V to Va; factor Xa and Va convert prothrombin to thrombin with phospholipid and calcium ion. Thrombin converts fibrinogen to fibrin and factor XIII to XIIIa which in presence of calcium ion stabilizes the fibrin into crosslinked fibrin.

In case of extrinsic system factor VII converts to VIIa with tissue factor and calcium ions. The factor VIIa converts factor X to Xa with similar interactions as described above and further reactions follow as in the intrinsic cascade system. The nature of the protein adsorbed may also affect the activation of blood coagulation, complement and fibrinolytic system. It is also now known that receptors of fibrinogen exist on the platelet surface. Therefore platelets adhere where they find fibrinogen (Marguerie *et al* 1979); these receptors are available to fibrinogen when ADP is added to a platelet suspension. Therefore much attention has been paid in our laboratory to understand fibrinogen adsorption onto various substrates in comparison to albumin.

The complexity of blood–material interactions at the interface is depicted in figures 1 and 2. Table 1 lists the blood coagulation factors.

Lyman *et al* (1965) studied several polymer surfaces and evaluated their critical surface tension (γ_c) and surface free energy (γ_s) using contact angle data determined by the method of Zisman (1964). While the initial studies showed a relationship between the rate of clotting and γ_s , later studies indicated that this relationship does not hold rigorously, probably because of the heterogeneity of the surface.

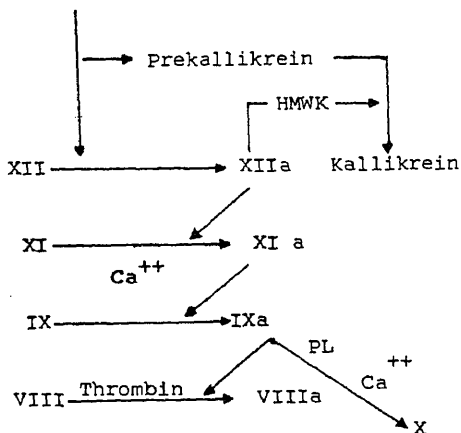
Andrade *et al* (1973) postulated that material surfaces which tend to have an interfacial energy of zero will be highly thromboresistant. The fact that materials

Table 1. Coagulation factors.

Factor	Name
I	Fibrinogen
II	Prothrombin
III	Thromboplastin
IV	Calcium ion
V	Proaccelerin
VI	Not assigned
VII	Proconvertin
VIII	Antihæmophilic factor
IX	Christmas factor
X	Stuart factor
XI	Plasma thromboplastin antecedent
XII	Hageman factor
XIII	Fibrin stabilizing factor

Intrinsic System

Surface Contact



Extrinsic System

Ca⁺⁺ VII Tissue factor

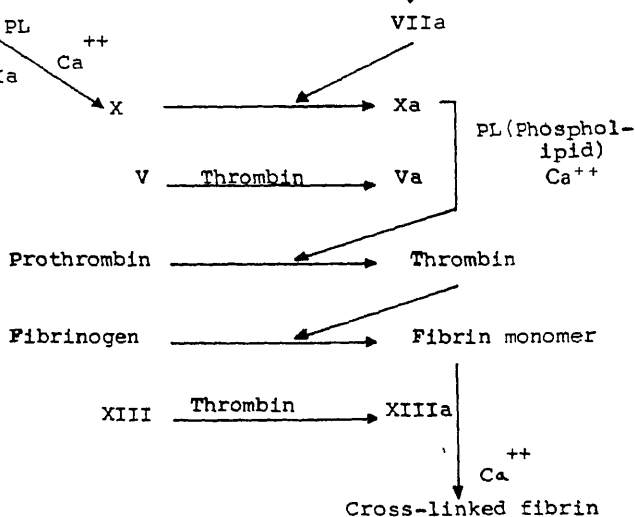


Figure 1. Blood coagulation cascade.

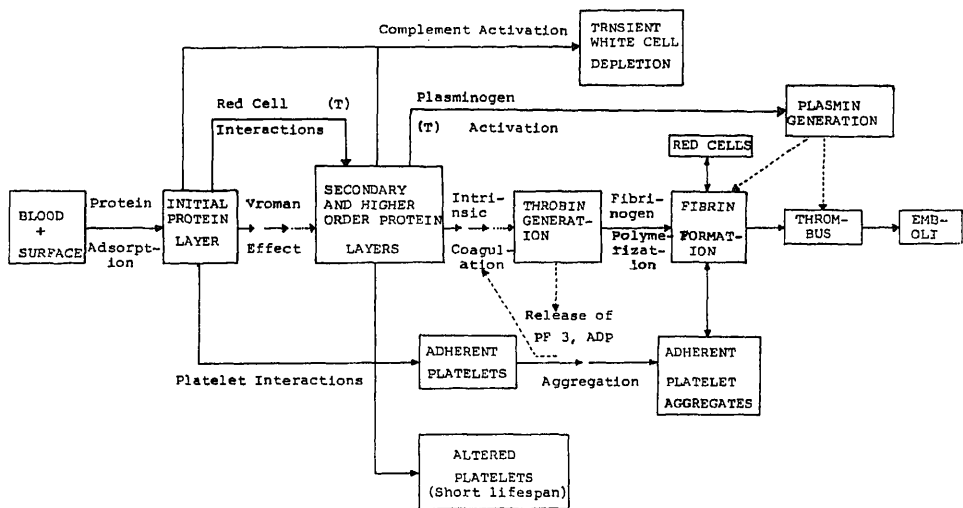


Figure 2. Blood-material interaction sequence.

with a minimal interfacial energy like hydrogels do possess a relatively low thrombus adherence enhances the validity of this hypothesis. Similarly the surface free energies of many polymers have been calculated by contact angle measurement. It was observed that a polymer having a critical surface tension of around 20–30 dynes/cm is highly blood-compatible (Baier *et al* 1970), but exceptions have been reported as in LTI carbons ($\gamma_c \approx 50$ dynes/cm). Further it has been indicated that dispersion $\alpha_s = \sqrt{\gamma_s^d}$ and polar $\beta_s = \sqrt{\gamma_s^p}$ components of polymer surfaces play an important role in interfacial interactions. It was found that low-dispersion, high-polarity surfaces, typified by surface-treated stillite 21 with $\alpha_s = 5.0(\text{dynes/cm})^{1/2}$ and $\beta_s \geq 5.0(\text{dynes/cm})^{1/2}$, provide surface energies that appear to favour weak adsorption and retention of plasma proteins, i.e. a poor surface from the compatibility point of view. Again, high-dispersion, low-polarity implants, e.g. LTI carbon with $\alpha_s \geq 6.0(\text{dynes/cm})^{1/2}$ and $\beta_s \leq 2.0(\text{dynes/cm})^{1/2}$, provide surface energetics favouring stable plasma protein retention, i.e. an excellent surface for blood compatibility (Kaelble and Moacanin 1977). For LTI carbons α_s and β_s values are $7.38(\text{dynes/cm})^{1/2}$ and $2.04(\text{dynes/cm})^{1/2}$. Sharma (1980) suggested an optimum α_s of $4.7(\text{dynes/cm})^{1/2}$ and β_s of $3.0(\text{dynes/cm})^{1/2}$ for a possible blood-compatible surface based on experimental observations and theoretical calculations as depicted in table 2. Such surfaces seem to adsorb albumin preferentially on the basis of the dispersion and polar components of the protein interacting with the surface.

The dispersion α_s and polar β_s components can be determined for any substrate as suggested by Kaelble and Moacanin (1977) as follows:

$$\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p = \alpha_s^2 + \beta_s^2,$$

$$\gamma_{LV} = \gamma_{LV}^d + \gamma_{LV}^p = \alpha_L^2 + \beta_L^2.$$

Adhesion energy, which is basically a measure of interface bonding, is given by

$$W_{SL} = \gamma_{LV}(1 + \cos\theta_L) \leq 2\gamma_{LV},$$

Table 2. Surface free energy components for various polymers.

Polymer	α_s	β_s	γ_s	γ_c	γ_{ij}
Silastic rubber (SR)	4.4	3.0	28.4	25.5	17.2
SR (Cast) - air	4.6	2.1	25.6	24.0	25.4
SR (Cast) - FEP	4.6	2.1	25.6	24.0	25.4
Polyethylene	5.15	2.0	30.5	33.0	26.7
Polypropylene	5.1	1.75	29.0	30.0	29.3
TPX	5.1	2.0	30.0	25.0	26.6
2025 - air	5.2	2.3	32.3	31.5	23.7
2025 - glass	5.15	2.8	34.3	31.5	19.0
1025 - air	4.9	3.3	34.9	31.5	14.8
1025 - glass	4.9	3.5	36.3	31.5	13.4
710 - air	5.15	2.85	34.6	31.5	18.7
710 - glass	5.15	2.75	34.1	31.5	19.5
Biomer - air	4.8	3.2	33.3	25.0	15.5
Biomer - glass	4.8	3.2	33.3	25.0	15.5

TPX, 4-methyl poly - pentene - 1

Block copolymer urethane ureas were based on polypropylene glycols of MW 2025, 1025, 710.

where θ_L is the contact angle of various organic solvents on the substrates.

$$W_{SL} = 2[\alpha_s \alpha_L + \beta_s \beta_L],$$

$$\frac{W_{SL}}{2\alpha_L} = \alpha_s + \beta_s \left[\frac{\beta_L}{\alpha_L} \right].$$

Thus $\left[\frac{W_{SL}}{2\alpha_L} \right]$ vs $\left[\frac{\beta_L}{\alpha_L} \right]$ is plotted as a straight line with intercept α_s and slope β_s . Since α_s and β_s are square roots of dispersion γ_{sv}^d and polar γ_{sv}^p parts of γ_{sv} , these components can be evaluated.

Kaelble (1976) further summarized the general concept for regular adsorption bonding in interfaces in the following relation for interfacial tension:

$$\gamma_{ij} = (\alpha_i - \alpha_j)^2 + (\beta_i - \beta_j)^2 + \Delta_{ij}.$$

Subscripts denote interactions from phase i and j interfaces dominated by van der Waals interactions which are termed as regular interfaces and the values of the term Δ_{ij} describe interdiffusion or ionic covalent interactions, which can be considered negligible. Thus from known values of α and β , γ_{ij} values for substrate - protein system can be evaluated as given in table 3.

From table 3 it seems that the interfacial tension is lowest with albumin in both the cases, viz model surface and LTI carbon, compared to fibrinogen and γ -globulin. However, LTI carbon with high dispersion and low polar components may interact with all proteins under consideration quite intensely, unlike the case of the model surface, where both the dispersion and polar components appear to be taking an active part in the interaction process for albumin. On the other hand polar components are playing a predominant role in case of fibrinogen and γ -globulin. So a

Table 3. Interfacial energy parameters for different proteins and for platelets.

Protein	Polar non-polar ratio	α_i [(dynes/cm) ^{1/2}]	β_i [(dynes/cm) ^{1/2}]	Model substrate ^{a,c}		LTI carbon ^{b,c}	
				γ_{ij} (dynes/cm)	$\frac{(\beta_i - \beta_j)}{(\alpha_i - \alpha_j)^2}$	γ_{ij} (dynes/cm)	$\frac{(\beta_i - \beta_j)^2}{(\alpha_i - \alpha_j)^2}$
Fibrinogen	1.626	4.97	6.35	11.27	151.3	24.39	3.5
γ -Globulin	1.205	5.43	5.96	9.30	16.8	19.20	4.4
Albumin	1.072	5.60	5.79	8.64	9.6	17.30	4.4
Platelets	2.604	4.40	7.10	16.90	186.8	34.48	2.0

^aFor values of $\alpha_j = 4.7$ (dynes/cm)^{1/2} and $\beta_j = 3.0$ (dynes/cm)^{1/2}

^bFor values of $\alpha_j \approx 7.38$ (dynes/cm)^{1/2} and $\beta_j = 2.04$ (dynes/cm)^{1/2}

^cThe ratio indicates relative contribution of polar to dispersion components toward interfacial energy for the various proteins and for platelets compared for the same surface.

possibility of weak adsorption of these proteins is suggested on this surface relatively (Sharma 1984). In case of LTI carbons, which may interact with all the proteins under discussion equally intensely, taking dispersion and polar components of the proteins into account, no preferential adsorption may be possible. Therefore availability of a particular protein may also be an important parameter in this case. Since albumin content is much higher in blood compared to other proteins, an increased adsorption of albumin on LTI carbons is suggested. Further, albuminated surfaces, as discussed earlier, usually reduce the adhesion of platelets and enhance the blood compatibility. So this may certainly be one of the reasons why LTI carbons are also blood-compatible. Similarly the cell or microbial adhesion onto non-proteinated model surface and LTI carbon can be explained relatively. For example, the dispersion α_p and polar β_p components for platelets has been evaluated (Sharma 1991) to be 4.4 (dynes/cm)^{1/2} and 7.1 (dynes/cm)^{1/2} as shown in table 3. Obviously, for LTI carbons, there is no preferential adhesion of proteins of platelets (cells), while on model surface, albumin adsorption is preferential even in comparison to platelets.

However, the adhesion of platelets onto various substrates is very complex and certainly not governed by a single specific parameter. It is observed with ¹²⁵I-labelled human fibrinogen or immunoglobulin G (IgG) that the adsorption of fibrinogen and IgG were greater on polyacrylonitrile than on cuprophane. However, fibrinogenated polyacrylonitrile does not promote the adhesion of ⁵¹Cr-labelled platelets or polymorphonuclear leucocytes. This may be due to either the direct involvement of fibrinogen-active sites in the interaction of the protein molecule with polyacrylonitrile or a conformational change in the fibrinogen molecule upon adsorption with respect to the surface energy components of the polymer (Chuang *et al* 1982). Further, fibrinogen has platelet adhering sites and these sites may have different energy parameters, compared to the rest of the segment, suitable to encourage the adhesion of platelets. The human fibrinogen molecule consists of three pairs of peptide chains joined by disulphide bridges. It is observed that platelet adhesion to polycarbonate (PC) substrates is inhibited by addition of fibrinogen factor 2b, ($A\alpha$, $B\beta$)₂ $\gamma\gamma$ ¹, with no significant difference between the effects of fraction 1a and 1b, i.e. ($A\alpha$, $B\beta$, γ)₂ chain composition. ADP-induced platelet binding to PC substrate also

decreases in presence of fraction 2b (Chandy and Sharma 1987). This may be due to the nonavailability of binding sites on this molecule or because a conformational change in the COOH terminus of the γ chain or γ^1 chain causes a change in fibrinogen conformation itself. On many materials, when blood comes in contact, instant adsorption of fibrinogen takes place, along with activatable clotting factors. Mainly HMWK will displace fibrinogen film within a few minutes. This is difficult in narrow spaces and if dilution is affecting concentration of HMWK or surface-activated blood with insufficient intact HMWK to remove the fibrinogen deposited. In such cases platelet adhesion is promoted. Perhaps while platelets race with fibrinogen/HMWK interactions, granulocytes race with γ -globulin plasma protein interaction of a similar nature (Vroman 1984–85). It is also observed that the incubation of pure fibrinogen in presence of a trace of plasminogen or plasma considerably enhances the plasmin-induced degradation of adsorbed fibrinogen (Brash *et al* 1985). Further, platelets, cells and proteins tend to have a net negative zeta potential of -8 to -13 mV (Sawyer and Pate 1953). If the surface is not highly charged, certain proteins, preferably albumin, may be adsorbed and form a passivating layer, which may ultimately make the material less adverse toward blood components and hence relatively more blood-compatible. For highly charged surfaces, even if protein adsorption does not take place, blood components may still suffer damage. For example, activated platelets may aggregate as microemboli and deposit in various organs causing the implant unsuccessful in the long run (Sharma 1991). Further, there also appears to be a relationship between complement activation and leucopenia occurring in haemodialysis with cellulose membranes. It seems that leucocyte adhesion is mediated by complement components. Complement activation via the alternative pathway, when blood comes in contact with implant with activation of C_3 and C_5 to C_{3a} and C_{5a} respectively, which induce mast cell degranulation resulting in histamine release, also stimulates cytokine (interleukin 1) release from monocytes. Along with cytokine leukotriene B_4 (LTB_4) and platelet activation factor (PAF) enhanced cell adhesion is brought about (including even neutrophil endothelial cell adhesivity). This encourages the formation of superoxide anion, H_2O_2 , OH etc; along with collagenase, elastase, gelatinase etc. These products may inhibit the reendothelialization of blood-contacting surfaces. It is believed that tissue necrosis factor (TNF) from activated neutrophils also plays an important role in the above process. The understanding of the above concepts is still not complete.

An attempt was made to further understand blood-material interaction by preparing surfaces having similar surface energy by grafting various hydrogels onto Angioflex via ^{60}Co irradiation (Hari and Sharma 1991) as indicated in table 4. It is obvious from the results that the polyethylene glycol-grafted substrate demonstrated not only adsorption of albumin but also less adhesion of platelets. This reflects the relevance of chemical nature of the substrate besides surface free energy parameters. Further, blood-compatible surfaces do not induce morphological changes in platelets (pseudopods), release of serotonin, ADP and platelet factor (PF_4), etc. Platelets may lose their shape slightly, but come back to original shape if reflected from the substrates (Hari and Sharma 1993).

A similar phenomenon is obvious on biologically modified surfaces as shown in table 5. While octane contact angles are similar, platelet adhesion is low on certain substrates depending upon biological activity.

From the above discussion one can conclude that both physicochemical and

Table 4. Platelet adhesion, amount of proteins adsorbed after 3 h exposure, and surface free energy (γ_{sv}) of Angioflex surfaces grafted with various hydrogels.

Surface	γ_{sv}	No. of platelets adhered/mm ²	Surface conc. of ($\mu\text{g}/\text{cm}^2$) $\pm$ S.D.	
			Albumin	Fibrinogen
Bare Angioflex	30.98	12.3 $\pm$ 2.3	1.209 $\pm$ 0.17	0.662 $\pm$ 0.11
Gamma irradiated*	32.10	10.0 $\pm$ 2.8	1.046 $\pm$ 2.17	0.697 $\pm$ 0.11
PHEMA grafted*	35.64	4.5 $\pm$ 2.0	1.522 $\pm$ 0.15	0.718 $\pm$ 0.12
Polyacrylonitrile grafted*	35.47	5.0 $\pm$ 1.8	1.543 $\pm$ 0.14	0.800 $\pm$ 0.12
Polyacrylamide grafted*	35.05	5.3 $\pm$ 2.0	1.330 $\pm$ 0.11	0.646 $\pm$ 0.12
PEG grafted*	35.50	2.8 $\pm$ 1.8	1.270 $\pm$ 0.32	0.568 $\pm$ 0.06
Bare PEUU	—	6.2 $\pm$ 2.0	0.280	0.240
PE grafted**	—	1.4 $\pm$ 1.0	0.290	0.250

*On Angioflex surface

**Polyelectrolyte (PE) with sulphamate and carboxylate groups like heparin developed from natural rubber (on PEUU surface)

Table 5. Octane contact angle and platelet adhesion to various modified chitosan membranes.

Membrane	Octane contact angle (degrees)	Adhered platelets per mm ² $\pm$ S.D.
Albumin-blended chitosan membrane (ACM)	138.2 $\pm$ 2.44	17.7 $\pm$ 2.00
ACM + liposome (+ ve)	134.1 $\pm$ 2.70	25.7 $\pm$ 2.60
ACM + lip. (+ ve) + hirudin	141.3 $\pm$ 1.60	12.5 $\pm$ 2.00
ACM + lip. (+ ve) + PGE ₁	122.3 $\pm$ 3.17	8.3 $\pm$ 1.80
ACM + lip. (+ ve) + AT-III	138.5 $\pm$ 1.44	11.7 $\pm$ 1.90
ACM + lip. (+ ve) + heparin	137.1 $\pm$ 1.81	10.5 $\pm$ 2.10
ACM + liposome (− ve)	141.4 $\pm$ 2.30	15.0 $\pm$ 2.3
ACM + lip. (− ve) + hirudin	143.7 $\pm$ 2.10	10.2 $\pm$ 1.98
ACM + lip. (− ve) + PGE ₁	133.4 $\pm$ 2.07	5.9 $\pm$ 1.95
ACM + lip. (− ve) + AT-III	143.6 $\pm$ 2.06	9.8 $\pm$ 1.93
ACM + lip. (− ve) + heparin	144.2 $\pm$ 1.35	9.3 $\pm$ 1.91

AT-III, antithrombin III.

biological aspects are important while considering blood–material interaction with an objective of developing blood-compatible material surfaces. Surface modification by immobilizing antithrombin III, PGE₁ and methyldopa complex on albuminated substrates has also been attempted, which demonstrated enhanced albumin adsorption compared to bare PC surface (Chandy and Sharma 1989). Similarly aspirin, vitamins, antibiotics, anaesthetics, antihypertensive drugs, etc seem to encourage albumin adsorption in varied degree and also reduce platelet adhesion. This could

be important information from the clinical point of view for patients having an artificial internal organ (Sharma 1991).

Usually in case of polymers the denatured protein-polymer-water system represents a lower energy system than the original state. In case of metals, whether or not an oxide layer is present, there is a large electric field. Small ions accumulate, lowering the strength of the field, but there is a great advantage in replacing these with protein molecules. The dipole moment of a protein is very much greater than that of a small ion and there is a gain in entropy on replacing several small ions by one large molecule. However, denaturation of a protein is not normally experienced in electric fields as the possible loss of free energy is increasing further the dipole moment is rarely greater than the gain due to exposure of the hydrophobic core. Electrostatic and hydrogen bond interactions are other major forces that bind proteins depending upon microenvironment.

Protein adsorption studies on various metal surfaces such as Ti, Al and Ta have been carried out as shown in table 6. It is interesting to note that after a certain optimum thickness Al (500 Å) and Ti (400 Å) become more blood-compatible, while Ta (200 Å) becomes tissue-compatible based on Fib/Alb mole ratio (table 6).

Table 6. Protein adsorption onto titanium, tantalum and aluminium with oxide layer of varied thickness.

Surface	Water contact angle (degrees)	Protein adsorbed in 3 h ($\mu\text{g}/\text{cm}^2$)		Mole ratio Fib/Alb
		Albumin	Fibrinogen	
I. Titanium ¹				
(a) Cleaned and glow discharged	21.4 + 1.4	0.037	1.086	5.64
(b) With 266 Å oxide layer	109.3 ± 1.8	0.215	1.629	1.44
(c) "408 Å"	117.0 ± 3.2	0.180	1.080	1.14
(d) "1268 Å"	136.3 ± 6.1	0.174	0.876	0.69
II. Tantalum ²				
(a) Cleaned and glow discharged	Spreading	0.224	0.228	0.186
(b) With 200 Å oxide layer	60.1 ± 2.9	0.127	0.272	0.391
(c) "500 Å"	50.4 ± 2.9	0.193	0.295	0.279
(d) "960 Å"	40.2 ± 5.7	0.248	0.388	0.286
III. Aluminium ³				
(a) Cleaned and glow discharged	Spreading	0.041	0.060	0.268
(b) With 50 Å oxide layer	26.2 ± 7.8	0.065	0.120	0.338
(c) "350 Å"	33.1 ± 2.2	0.072	0.130	0.331
(d) "500 Å"	34.2 ± 6.6	0.089	0.140	0.288
(e) "840 Å"	31.7 ± 4.7	0.070	0.130	0.340

1. Sunny and Sharma (1991)

2. Sharma and Paul (1992)

3. Sunny and Sharma (1990); Sharma and Sunny (1990)

Problems related to T-cell defects cause autoimmune disease due to overproduction of antibodies by B-cells (up to two to three times more than normal). To help such patients, usually the blood is fractionated via plasmapheresis and plasma is passed through a perfusion column where selected adsorption of pathogenic immunoglobulins occurs. After passing through this column the plasma along with other blood components is passed into the patient. An attempt was made utilizing polyvinyl alcohol (PVA), chitosan, polyacrylamide (PAA) and hydroxyapatite (HA) (200–400 μ) beads modified with amino acids such as tryptophan and phenylalanine for selective adsorption of immunoglobulins from whole blood if possible. The results appear to be encouraging as shown in table 7.

Since bone consists of collagen and HA (60–70%), the latter, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, was synthesized from $\text{Ca}(\text{OH})_2$ and orthophosphoric acid H_3PO_4 as basic component. The microspheres of HA have also been developed by the simple procedure of mixing HA with chitosan in acetic acid and dropping this solution slowly into a polymer solution in toluene. By washing the spheres with toluene, acetone and distilled water and heating at 400°C, the coated chitosan was removed. Such microspheres, of varied sizes and shapes, under pressure with sintering for required porosity may be useful in various dental, orthopaedic and drug-delivery applications. HA–aluminachitosan microspheres have also been developed for similar applications.

Various materials such as PEUU, PVA, chitosan, etc have been used towards artificial-skin applications with and without collagen. *In vivo* experiments on rabbits (dorsal region) have been performed and relative healing has been evaluated as indicated in table 8. It is obvious that chitosan can be a very good substitute in artificial-skin application.

The basic problem with bioprosthetic heart valves such as porcine valve (Carpentier Edwards) and bovine pericardium valve (Ionescu-Shiley) has been calcification. However, by treating with Fe^{3+} or Al^{3+} solutions it seems that the process of calcification can be inhibited. Even cross-linking agents such as carbodiimide or glycerol etc instead of glutaraldehyde, reduce calcification. Prevention of calcification through FeCl_3 release from chitosan beads, coimplanted on subdermal pouches of rats, have been studied in our laboratory. It seems that an optimum combination of ferric and magnesium ions also reduces calcification. A beginning has also been made towards the use of chitosan along with liposome encapsulation systems for significant reduction of calcification in bioprosthetic valves.

Table 7. Immunoprotein adsorption from human plasma (GBS) on modified chitosan (CB), polyvinyl alcohol (PVA) and acrylamide (PAA) microspheres.

Protein	Pre-perfusion levels (mg/dL)	Post-perfusion level (mg/dL)			Percentage adsorbed		
		CB	PVA	PAA	CB	PVA	PAA
IgG	763.81	589.59	679.11	666.55	22.8	11.1	12.7
IgM	90.88	81.74	83.57	79.00	10.1	8.1	13.1
IgA	147.27	70.81	95.95	98.20	51.9	34.8	33.3
C ₃	200.06	162.86	139.04	176.30	18.6	30.5	11.9

Adsorption was for 3 h on 3 g of microspheres (bead size CB 400–600 μm). GBS, Guillain Barre syndrome (PAA and PVA 600–800 μm).

Table 8. Wound healing pattern in rabbits of different polymeric samples with various modifications.

Sample	Sterilization	No. of days taken for complete wound healing*
PEUU	Chemical	36.38 $\pm$ 3.90
PEUU + collagen + albumin	Chemical	25.15 $\pm$ 4.32
Albumin + epidermal growth factor	Chemical	24.39 $\pm$ 3.83
PVA	Chemical	34.87 $\pm$ 4.12
PVA + collagen + albumin	Chemical	38.10 $\pm$ 1.27
Chitosan	Steam	32.74 $\pm$ 5.23
Chitosan + collagen	Steam	24.93 $\pm$ 4.30
Chitosan + fibrin gel	Steam	28.81 $\pm$ 8.39

*Each value expressed as mean $\pm$ S.D. of three animals (6 wounds, 3 $\times$ 1.5 cm²)

4. Conclusion

Surface modification of implants plays an important role in enhancing blood and tissue compatibility. However, many surfaces may change after sterilization so emphasis should also be given to understanding sterilization-induced changes in the functioning of any prosthetic device, *in vitro* and *in vivo*, before review by an ethics committee for selection for limited clinical trials on humans.

Further, controlling the surface properties at the manufacturing stage alone is not enough because changes may come even at stages like handling, packaging and storage, besides sterilization, which can significantly modify the surface properties and ultimately the success of the implant.

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Trends in corrosion protection of materials

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Abstract. The rapid advances in technologies in various fields have also recorded significant progresses in the field of newer materials as the reliability and effective performance of industrial equipment as well as the associated components mostly depend upon their integrity over specified period.

Though the basic methods of protection of materials like use of corrosion-resistant alloys, application of surface coatings, modification of the environment and application of cathodic protection have largely remained the same, the approaches and techniques adopted in each of these fields have been so advanced that one could today advocate appropriate protection systems with high reliability and performance.

The author presents some of his contributions along with his colleagues in the fields of cathodic protection of vital structures, development of newer coatings for specific applications and new approaches to corrosion monitoring techniques, besides highlighting the corrosion behaviour of some of the heat-treated alloys which are specifically used in such strategic areas as space and defence.

The presentation would also cover briefly some of the techniques that have been employed by the author for better understanding of corrosion and passivation of metals and alloys.

Keywords. Corrosion protection; materials.

1. Corrosion audit and corrosion control

Corrosion audit and corrosion control have become the watchwords of the major industrial sectors in view of their major impact on the performance and capacity of industrial plants. It is being increasingly realized that application of the existing knowledge on corrosion control alone can bring about substantial savings in the cost of maintenance and repair, besides ensuring quality products with minimum financial inputs.

Corrosion of metals and alloys is still controlled by conventional methods like application of surface coatings, use of inhibitors, application of electrochemical protection methods, besides the use of more corrosion-resistant materials for specific applications. However, better understanding of corrosion processes and also the techniques involved in control of the same have led to the use of more efficient methods at less cost. The current presentation will highlight some of the achievements of the author in collaboration with colleagues in various aspects of the development of anti-corrosion technologies as well as the understanding of the mechanism of corrosion and passivation.

2. Electrochemical protection

Cathodic protection and anodic protection are being increasingly employed in industries for control of corrosion of highly corrodable steel in typical environments at low costs. These methods obviously avoid the use of other, costlier methods like

surface coatings and inhibitors, though a combination of these techniques would be more economical and beneficial in many cases. Of the two methods, cathodic protection is more widely employed, as this is based on bringing about immunity to corrosion through understanding the thermodynamics of corrosion processes. Moreover, this method is practicable under almost all conditions where cathodic polarization can be achieved at optimum current densities.

Anodic protection, on the other hand, is based on the ability of the metal or alloy to get passivated in the given medium, when polarized over a fairly wide range of anode potential. This would immediately suggest that this method can be employed only in cases where anodic passivation is economically feasible. This type of protection is, however, employed in chemical and engineering industries for the protection of steel and stainless steel in acids and a few other processing chemicals. CECRI has designed an anodic protection system¹ with the automatic control of potential for sulphuric acid heat-exchangers made of either steel or stainless steel. Extensive studies were carried out to evaluate the design parameters like critical current, passivation current and the potential range of the passivation under different conditions of concentration of acids, temperature and velocity, and these were the main inputs for the above design.

3. Cathodic protection

Cathodic protection is the only foolproof method of protection of inaccessible structures like underground pipelines and marine structures like offshore platforms and rebars in concrete, apart from industrial equipment like heat-exchangers in chemical industries. Though cathodic protection can be achieved either by sacrificial anode or impressed current system, the choice is obviously based on economics as well as practical considerations.

CECRI has, over the years, developed the total technology for cathodic protection contributing to the development of galvanic anodes, impressed current anodes, and automatic control and monitoring system, besides providing technical assistance to various industrial sectors on the design of cathodic protection for industrial structures.

3.1 Galvanic anodes

The three major types of galvanic anodes based on aluminium, magnesium and zinc have been extensively studied, leading to the development of the above anodes which are already in commercial production in the country. These anodes have shown better performance in terms of improved anode efficiency and more uniform self-corrosion.

3.2 Impressed current anodes

Though various types of impressed current anodes are in vogue, CECRI has, for the first time, employed the TSIA, developed at CECRI for the chlor-alkali industry for use in cathodic protection of marine structures, replacing the conventional lead-antimony-silver alloy anodes. The TSIA have performed extremely well during the past five years since their installation and are still performing well. It is hoped

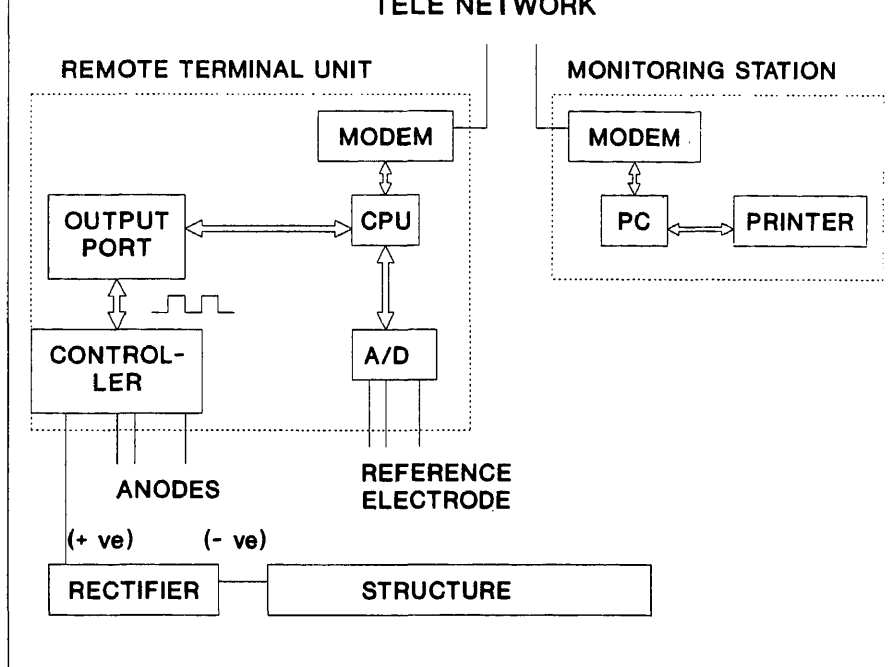


Figure 1. Block diagram of automatic control system for cathodic protection.

that these types of anodes, costing and weighing less than conventional anodes, would be more widely employed for the protection of both underground and marine structures. As an experimental measure, CECRI has made use of the same anode for the protection of agricultural tubewells in Tamil Nadu. The other development of CECRI in anodes for chlorate industries, viz. the lead dioxide coated graphite electrode, was also tested successfully for use in cathodic protection of underground structures.

CECRI has evolved, through the years, different types of automatic control systems for cathodic protection starting from the use of SCR to the use of SCADA, the most recent development. The supervisory control and data acquisition (SCADA) system helps in the remote monitoring and control of cathodic protection system, either through telephone networks or through satellite communication (figure 1). The system has its own software package for control, monitoring, diagnosis of faults and also acquisition of data with facilities to monitor 16 points (reference electrodes) at the same time. The above SCADA has already been tested in the field for the protection of jetties at Madras Port Trust and was also demonstrated to officials of the Oil and Natural Gas Commission (ONGC) by connecting it to satellite communication. The main advantage of this system is that it uses a pulsed current as a result of which the potentials could be measured and controlled during off-stage, eliminating the IR drop, which usually causes error in measurement in conventional methods. It is hoped that this system would be widely used in the near future in the country for the protection of long oil pipelines as well as strategic marine structures.

4. Development of coatings

Surface coatings have been occupying a key position as a major method of corrosion control in the industrial world. It is estimated that 40% of the cost of corrosion control is accounted for by this method. The three components that are involved in the realization of the best performance for any coating system include a clean and good surface, use of the most appropriate painting system, and the proper method of application, including the period of application. CECRI has done considerable work in all these fields and has developed a few anti-corrosive primers^{6,7}, rust converters⁸ and rust converting primers^{9,10} and coatings for specific applications like high-temperature resistance¹¹, radiation resistance¹², chemical resistance, etc.

4.1 Conversion coatings

Conversion coatings have played a major role in surface preparation as well as in providing temporary protection. Chromic acid has been the cheapest and the most efficient chemical used in the passivation of non-ferrous metals like aluminium, zinc and cadmium. However, environmental regulations have put a stop to the use of these toxic chemicals in all their applications including inhibitors and primers. CECRI has been able to develop a non-chromate formulation for passivating zinc and aluminium¹³, making them suitable for subsequent painting or making them appear better temporarily for consumer applications. This method is based on the use of other oxidation agents like permanganate, molybdate, etc. in combination with other activating agents.

5. Water-treatment chemicals

Water is used in many industries for various applications such as steam generation, cooling, secondary recovery of oils and pressure testing of equipments. Water used for these purposes has to be properly treated for keeping the extent of corrosion to acceptable levels, besides eliminating the possibility of scale formation. Formulations avoiding chromate and toxic biocides have been developed by CECRI as a total package for various industrial uses.

In this context, it should be mentioned that control of fouling and biocorrosion plays a major role in the performance of heat exchangers. Systematic investigations have been carried out for identifying the effective biocide and also for monitoring the same in industrial conditions¹⁴.

6. Corrosion behaviour of some heat-treatable alloys

The corrosion resistance of heat-treatable alloys depends upon the heat treatment condition. Corrosion resistance is maximum when the material is in solution heat treated condition. Aging (heat treatment) decreases corrosion resistance. This is due to the formation of precipitates during aging which makes the material heterogeneous. The corrosion behaviour of the material is dependent upon the aging condition—whether the material is underaged, peakaged or overaged. The results of the investigations

Table 1. Effect of heat treatment on corrosion behaviour.

Type of heat treatment	Heat treatment condition	Corrosion current by polarization technique ($\mu\text{A}/\text{cm}^2$)	$R_{ct}(\text{K}.\text{ohm}.\text{cm}^2)$ by impedance technique
Solution annealed	—	0.15	> 30
Underaged	450°C, 4 h	3	3.1
Peakaged	450°C, 5 h	3.3	2.2
Overaged	450°C, 7 h	2	4.3

Table 2. Effect of electropolishing on corrosion behaviour.

Type of heat treatment	Heat treatment condition	Corrosion current by polarization technique ($\mu\text{A}/\text{cm}^2$)*	$R_{ct}(\text{K}.\text{ohm}.\text{cm}^2)$ by impedance technique
Underaged	450°C, 4 h	0.18 (3)	36 (3.1)
Peakaged	450°C, 5 h	0.18 (3.3)	32 (2.2)
Overaged	450°C, 7 h	0.13 (2)	80 (4.3)

* Values in parentheses correspond to those in table 3.

Table 3. Pitting corrosion behaviour of stainless maraging steel.

Type of heat treatment	Heat treatment condition	Pitting potential (mV) vs SCE	Protection potential (mV) vs SCE
Underaged	450°C, 4 h	+ 50	— 75
Peakaged	450°C, 5 h		
Overaged	450°C, 7 h	+ 250	0
<i>Effect of electropolishing</i>			
Underaged	450°C, 4 h	+ 650	+ 650
Peakaged	450°C, 5 h	+ 660	+ 660
Overaged	450°C, 7 h	+ 750	+ 750

Table 4. Constant load SCC test data.

Aging	Time to failure (h)
Underaged (450°C/4 h)	10–13
Overaged (450°C/7 h)	324

Stress : 80% of proof stress
Medium : 5% NaCl solution

carried out on some heat-treatable alloys—stainless maraging steel in chloride environments¹⁵, 7020 aluminium alloy in N_2O_4 environment and AA 6061 aluminium alloy¹⁶ in humid environment—are presented in this paper.

6.1 Corrosion behaviour of stainless maraging steel

The effect of heat treatment on the corrosion behaviour of stainless maraging steel and also the effect of electropolishing on the corrosion behaviour are given in tables 1 and 2. It may be seen that overaging for 7 h which produces the same hardness as underaging in 4 h gives rise to lower corrosion, higher pitting potential and better resistance to stress corrosion cracking (tables 1–4).

6.2 Corrosion behaviour of 7020 Al alloys for N_2O_4

The studies carried out at CECRI have indicated that the general as well as stress corrosion behaviour of this alloy can be reasonably monitored by choosing the appropriate weld metals, as shown in table 5.

Table 5. Corrosion rates of the 7020 parent metal and welds after 30 days of immersion in liquid N_2O_4 .

Parent metal/weld with filler metal	Rate (mmpy)
Parent metal	0.004
AG 4.5 Mn	0.006
AG 4Z2	0.004
AG 5	0.040

Table 6. Cleaning efficiency of various baths.

Composition of cleaning solution	Temperature (°C)	Duration (min)	Rate of attack (μm)	Remarks
4% NaOH	30	2	1.13	Black stains remain
10% H_3PO_4	30	15	1.03	Clean
Sodium hydroxide (4%) + sodium metasilicate (1.45%)	30	15	0.85	Partly cleaned
3% CrO_3 + 10% H_2SO_4	85	2	2.14	Clean surface
50% HNO_3 (1:1)	30	15	0.2	Stains not removed completely
50% HNO_3 (1:1)	30	60	1.02	Stains completely removed

Table 7. Performance of coated 6061 aluminium alloy in accelerated condensation test (RH 100% at 50°C).

Type of treatment	Time to stain	Surface appearance after 30 days
Without treatment	30 min	Severely stained
Permanganate	Pits initiated in 5 days	Severely pitted
Molybdate	5 days	Severely stained
Chromate	30 days	Not affected
Passivation treatment by HNO ₃ (50% HNO ₃ for 1 h)	2 days	Staining initiated

The stress corrosion test carried out by 4-point loading over 100 days as well as the constant load test for 6 h have indicated that AG4Z2 weld metal had higher resistance than the other weld materials.

3 Staining of 6061 alloy in humid environments

The causes for the staining of these alloys which are used as fuel containers were examined and methods of removal of such stains as well as control of formation of such stains through the formation of various types of conversion coatings were demonstrated (table 7).

Corrosion control in concrete structures

Concrete structures were expected to last for a minimum of 100 years as either deterioration of concrete or corrosion of rebars in an alkaline environment was not anticipated. However, failures of major concrete structures in such short spans of time as five years have been reported from all over the world.

CECRI has been giving a lot of attention to the causes and the mechanism of corrosion of concrete structures since the 1960s and these studies have led to the development of a number of anti-corrosion technologies and techniques for monitoring corrosion. The former includes the development of protective coatings for rebars based on cement slurry and inhibitors¹⁷ which have been made mandatory for all major bridges and other constructions in the country by the Ministry of Surface Transport (MOST). This technology which has been released to more than 10 industries has now been superseded by the development of a cement-polymer composite coating¹⁸. This has specific advantages over other coatings. This coating can be applied also on rusty steel. It can be applied in the shop and is suitable for use in prestressing steel wires also.

The causes and extent of deterioration of concrete as well as the corrosion of rebars in different environments have been extensively studied. These studies have led to the development of appropriate technologies for rehabilitation of the distressed structures. Another major contribution of CECRI in this field has been the develop-

ment and use of techniques for monitoring corrosion of rebars and prestressing steel wires. Resistivity measurement for characterizing the quality of concrete and also for evaluating the condition of prestressing steel wire, development of corrosion monitoring probes with appropriate data acquisition systems, and development of linear polarization technique for corrosion rate measurement are worth mentioning as they are already being installed for continuous monitoring of the corrosion behaviour of major bridges in the country¹⁹.

8. Mechanistic aspects of corrosion

It is said that understanding the cause of the problem provides more than 50% of the answer to any corrosion problem. A number of electrochemical and physico-chemical techniques have been employed for understanding the mechanism of corrosion of metals and alloys in different environments. However, specific mention might be made of the use of rotating ring disk electrode for understanding the mechanism of selective dissolution of alloys²⁰, spectroelectrochemical investigations for characterizing the passive film, especially in terms of its composition and electronic behaviour²¹, and use of such techniques as noise analysis²² and impedance measurement^{23, 24} for rapid evaluation of corrosion behaviour of metals and alloys.

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Modelling high-temperature creep of anisotropic material

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Abstract. Cast single-crystal superalloys are being used as turbine blades in modern aeroengines with $\langle 001 \rangle$ axis oriented along the direction of principal stress. This allows use of higher operating temperature with associated improvement in efficiency. Although $\langle 001 \rangle$ is the natural direction of crystal growth in these alloys it is often not possible to attain perfect alignment. Consequently, besides time-dependent deformation this would induce a change in cross-sectional shape and crystal orientation of the blade as a result of service exposure. Therefore in order to exploit their full potential it is necessary to develop a predictive system which could model effect of crystallographic anisotropy on high-temperature creep deformation of such materials. The paper reviews the recent developments in this direction and suggests that modelling not only helps in identifying the dominant mechanisms of deformation but also suggests simple experiments to verify them.

Keywords. Superalloy; single crystal; octahedral/cube slip; deformation mechanism; orientation change; SRR99.

1. Introduction

The development of single-crystal superalloys and their introduction as turbine blades in aeroengines have been the major achievements in gas-turbine technology during the last decade. This also provides an example of how the anisotropic behaviour of materials could be exploited to improve the performance (or efficiency) of the engine by raising its safe operating temperature. It is reported that the use of single-crystal superalloys such as PWA 1480, SRR99 and CMSX2 offers at least 50°C higher temperature capabilities than those of conventionally cast or directionally solidified alloys (e.g. Mar M 200, Mar M 002). However, in order to exploit their full potential through the use of advanced computer-based design procedures it is necessary to characterize fully their anisotropic behaviour.

There have been several experimental studies on anisotropic creep behaviour of single-crystal superalloys. There is some controversy as to whether $\langle 001 \rangle$ or $\langle 111 \rangle$ crystal orientations are strongest. Caron *et al* (1988) have shown that γ' size and morphology can have a profound effect on both the magnitude and nature of this anisotropy. The mechanisms of deformation in γ' -strengthened superalloys can be very complex depending on the distribution of γ' and the conditions of deformation. Evidence of both octahedral slip having either $\langle 101 \rangle$ or $\langle 211 \rangle$ Burgers vectors and cube slip have been reported (Kear *et al* 1967; Caron *et al* 1988) after tensile deformation at 750–980°C. Clearly the extent of anisotropy will depend on the number and the type of operative slip systems. Ghosh *et al* (1990) proposed a model for simulating the creep behaviour of anisotropic material assuming this to be determined by shear deformation on various slip planes. An analysis of the creep curves of SRR99 over a range of stresses and temperatures using this approach indicates that creep in these alloys is controlled by both octahedral and cube slip. The present work describes the basic principles of modelling creep of single crystals and suggests simple experimental methods of identifying the operative slip system.

A series of papers from National Physical Laboratory, UK, and Cambridge University have described a model of creep deformation of isotropic engineering alloys based on the formalism of continuum damage mechanics. The most novel aspect of this approach is the replacement of the empirical equations of the type introduced by Kachanov (1958), Robonotov (1969) and Leckie and Hayhurst (1977) with explicit equations that are fully consistent with current understanding of deformation mechanism in engineering materials. The model has been incorporated in a software package called CRISPEN. Dyson and McLean (1990) recently reviewed its current status in describing creep behaviour of engineering alloys particularly those exhibiting substantial tertiary creep. Dyson and Ashby (1984) identified three broad categories of damage that can make significant contributions to tertiary creep. They are: (i) loss of external section due to geometrical changes leading to a change in stress under constant loading condition (ω_1), (ii) loss of internal load-bearing section due to cavitation or cracking which occurs commonly at grain boundaries (ω_2), (iii) changes in the material microstructure (e.g. dislocation density, particle size) that reduce the strength of the material (ω_3).

The damage parameter ω_i can be defined in a number of ways. Assuming that ω_i is a linear function of strain it can be shown that creep rate $\dot{\epsilon}$ is an exponential function of ω_1 and ω_2 (Dyson and Gibbons 1987; Dyson 1988). However, the effect of ω_3 has been represented as either a linear or an exponential dependence on creep rate (Dyson and McLean 1990).

In general the overall tertiary creep behaviour of superalloys should be determined by each of the above damage mechanisms. However, the situation is somewhat simpler in the case of single-crystal material. Since there is no grain boundary the effect of cavitation could be ignored ($\omega_2 = 0$). Similarly, if one were to look at constant stress creep data where the effect of decreasing cross-sectional area is compensated by proportionate load reduction, it is not necessary to consider the influence of ω_1 . Curtis *et al* (1993) analysed the constant stress-creep curves of SRR99 having $\langle 001 \rangle$ orientations using the isotropic creep model. It has been shown that beyond 750°C creep behaviour of the alloy can be adequately described by the linear damage model. Consequently the tertiary creep behaviour of single-crystal superalloys of a given orientation could be represented as

$$\begin{aligned}\dot{\epsilon} &= \dot{\epsilon}_i(1 + \omega), \\ \dot{\omega} &= C\dot{\epsilon},\end{aligned}\tag{1}$$

where $\dot{\epsilon}_i$ and C are material constants and ω_3 has been redesignated as ω .

Although this type of description is adequate to interpret and analyse creep curves of single-crystal superalloys having a symmetric tensile axis it cannot be applied to crystals of any arbitrary orientation. This is because deformation in a single crystal takes place through glide on specific planes along specific directions. As a result a nonsymmetric tensile axis would tend to rotate about a specific direction. An appropriate model is therefore expected to predict not only the creep strain but also the amount of rotation. Ghosh *et al* (1990) have given a detailed account of how the model described in (1) could be reformulated in terms of shear strains on a specific slip plane and direction. This in principle would allow prediction of crystal rotation.

In order to appreciate its full implication it is worth reexamining the basis of such a model.

The equation set (1) could be recast as follows to obtain an estimate of the magnitude of shear strain γ^K on the K th slip system:

$$\begin{aligned}\dot{\gamma}^K &= \dot{\gamma}_i^K (1 + \omega^K), \\ \dot{\omega}^K &= C^K \dot{\gamma}^K,\end{aligned}\quad (2)$$

where $\dot{\gamma}_i^K$ and C^K represent material parameters describing evolution of shear strain on the K th slip system and ω^K is the accumulated structural damage on the specific slip system. Solution of the above equation set gives us the magnitude of accumulated shear strain on a specific slip system. In order to model the overall deformation one needs to solve similar equations for all possible slip systems. The total macroscopic displacement (e_{ij}) arising out of slip deformation (or simple shear) taking place on a set of N slip systems is given by

$$e_{ij} = \sum_{K=1}^N \gamma^K b_i^K n_j^K, \quad (3)$$

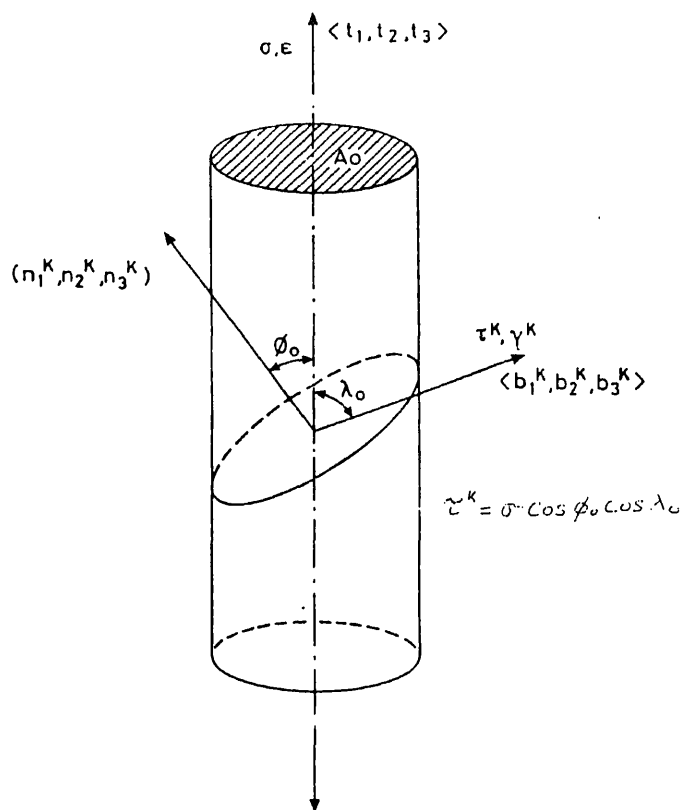


Figure 1. A schematic diagram showing the relationship of applied stress σ and tensile strain ϵ with slip plane (n_1^K, n_2^K, n_3^K) , slip direction $[b_1^K, b_2^K, b_3^K]$, resolved shear stress τ^K and shear strain γ^K .

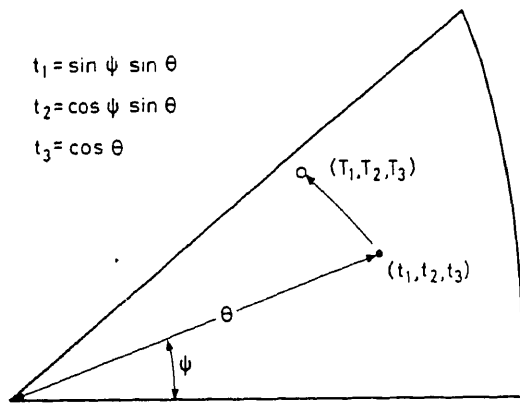


Figure 2. Schematic diagram showing the orientation relationship of an arbitrary tensile axis with various crystal directions before and after deformation.

where $[b_1^K, b_2^K, b_3^K]$ represents unit vector for the slip direction and (n_1^K, n_2^K, n_3^K) is the unit vector representing slip plane normal. Figure 1 gives a schematic representation of the orientation of the loading axis with respect to the slip plane normal and the slip direction. The angular location of the tensile axis $\langle t_1, t_2, t_3 \rangle$ has been shown with respect to three crystallographic axes of high symmetry, viz. $\langle 001 \rangle$, $\langle 011 \rangle$ and $\langle 111 \rangle$, on a stereographic triangle in figure 2. As a result of slip deformation the orientation of the tensile axis is likely to change. If $\langle T_1, T_2, T_3 \rangle$ is the vector representing the tensile axis after slip, then

$$T_i = (e_{ij} + \delta_{ij})t_j, \quad (4)$$

where $\delta_{ij} = 1$ for $i = j$ and $\delta_{ij} = 0$ for $i \neq j$.

The repeated subscript j in (4) represents summation over j from 1 to 3. Similarly any transverse direction in the crystal such as $\langle x_1, x_2, x_3 \rangle$ will change into $\langle X_1, X_2, X_3 \rangle$ and the relationship between the two is given by

$$X_i = (e_{ij} + \delta_{ij})x_j. \quad (5)$$

Consequently the longitudinal (ϵ) and transverse (ϵ_{tr}) strain could be calculated by

$$\epsilon = (\bar{T} - \bar{t})/\bar{t}, \quad (6)$$

$$\epsilon_{tr} = (\bar{X} - \bar{x})/\bar{x}, \quad (7)$$

where $\bar{X}$, $\bar{T}$, $\bar{x}$ and $\bar{t}$ represent magnitude of the respective vectors. The amount of rotation and the axis of rotation is also described by (4). The antisymmetric part of the matrix e_{ij} represents the rotation matrix (ω_{ij}) of the crystal. This is given by

$$\omega_{ij} = (e_{ij} - e_{ji})/2. \quad (8)$$

The magnitude $|\omega|$ and the axis of rotation are given by

$$|\omega| = \sqrt{\omega_{12}^2 + \omega_{23}^2 + \omega_{31}^2}, \quad (9)$$

$$\text{Rotation axis} = \frac{\omega_{23}}{|\omega|}, \frac{\omega_{31}}{|\omega|}, \frac{\omega_{12}}{|\omega|}. \quad (10)$$

Equations (2) to (10) describe completely the deformation behaviour of a single crystal at constant stress and temperature. In order to extend the model to allow interpolation or extrapolation over various stress and temperature ranges one needs to establish stress and temperature dependence of the material parameters γ_i^K and C^K . The procedure for establishing this has been discussed by Ghosh *et al* (1990). In subsequent part of the paper expressions used by Ghosh *et al* (1990) and the numerical values of these constants reported in table 3 of their paper have been used.

3. Results and discussion

Table 1 provides an illustrative calculation for the construction of displacement matrix of a single crystal with [001] as the tensile axis and {111} $\langle 1\bar{1}0 \rangle$ as the slip system. For such a case among 12 possible combinations of slip planes and slip directions eight have identical magnitude of resolved shear stress and the remaining four have no resolved shear stress component at all. Therefore eight of the 12 octahedral slip systems will contribute equally to the total creep strain at any instant of time. In this case γ represents the magnitude of shear strain on individual slip system whereas $\sigma/\sqrt{6}$ is the magnitude of resolved shear stress. The sum total of the displacement matrix as indicated in table 1 is symmetric signifying that there is no crystal rotation. The magnitudes of the tensile and the transverse strains are given by

$$\begin{aligned}\epsilon_{\langle 001 \rangle} &= \frac{8\gamma}{\sqrt{6}}, \\ \epsilon_{\langle 010 \rangle} &= \epsilon_{\langle 100 \rangle} = \frac{-4\gamma}{\sqrt{6}}.\end{aligned}\quad (11)$$

Since the magnitudes of transverse strain along two perpendicular directions are identical it may be concluded that the cross-sectional shape of the crystal remains unchanged.

However, the situation is quite different if the orientation of the tensile axis were more complex. For example, if it were $[\bar{1}23]$ deformation on only one of the 12 {111} $\langle 1\bar{1}0 \rangle$ slip systems having maximum resolved shear stress will dominate its response to creep. In this case the preferred slip system is (111) $[\bar{1}01]$. Therefore the displacement, strain and rotation tensors are given by

$$e_{ij} = \frac{\gamma}{\sqrt{6}} \begin{pmatrix} -1 & -1 & -1 \\ 0 & 0 & 0 \\ 1 & 1 & 1 \end{pmatrix}, \quad (12)$$

$$\epsilon_{ij} = \frac{\gamma}{\sqrt{6}} \begin{pmatrix} -1 & -1/2 & 0 \\ -1/2 & 0 & 1/2 \\ 0 & 1/2 & 1 \end{pmatrix}, \quad (13)$$

$$\omega_{ij} = \frac{\gamma}{\sqrt{6}} \begin{pmatrix} 0 & -1/2 & -1 \\ 1/2 & 0 & -1/2 \\ 1 & 1/2 & 0 \end{pmatrix}. \quad (14)$$

(111) [0 $\bar{1}$ 1]	$\begin{pmatrix} 0 & 0 & 0 \\ \bar{1} & \bar{1} & \bar{1} \\ 1 & 1 & 1 \end{pmatrix}^{1/\sqrt{6}}$	$\sigma/\sqrt{6}$	γ	
(111) [$\bar{1}$ 01]	$\begin{pmatrix} \bar{1} & \bar{1} & \bar{1} \\ 0 & 0 & 0 \\ 1 & 1 & 1 \end{pmatrix}^{1/\sqrt{6}}$	$\sigma/\sqrt{6}$	γ	$\frac{\gamma}{\sqrt{6}} \begin{pmatrix} \bar{1} & \bar{1} & \bar{1} \\ \bar{1} & \bar{1} & \bar{1} \\ 2 & 2 & 2 \end{pmatrix}$
(111) [1 $\bar{1}$ 0]	$\begin{pmatrix} 1 & 1 & 1 \\ \bar{1} & \bar{1} & \bar{1} \\ 0 & 0 & 0 \end{pmatrix}^{1/\sqrt{6}}$	0	0	

($\bar{1}$ 11) [101]	$\begin{pmatrix} \bar{1} & 1 & 1 \\ 0 & 0 & 0 \\ \bar{1} & 1 & 1 \end{pmatrix}^{1/\sqrt{6}}$	$\sigma/\sqrt{6}$	γ	
($\bar{1}$ 11) [0 $\bar{1}$ 1]	$\begin{pmatrix} 0 & 0 & 0 \\ 1 & \bar{1} & \bar{1} \\ \bar{1} & 1 & 1 \end{pmatrix}^{1/\sqrt{6}}$	$\sigma/\sqrt{6}$	γ	$\frac{\gamma}{\sqrt{6}} \begin{pmatrix} \bar{1} & 1 & 1 \\ 1 & \bar{1} & \bar{1} \\ \bar{2} & 2 & 2 \end{pmatrix}$
($\bar{1}$ 11) [110]	$\begin{pmatrix} \bar{1} & 1 & 1 \\ \bar{1} & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix}^{1/\sqrt{6}}$	0	0	

($\bar{1}\bar{1}$ 1) [101]	$\begin{pmatrix} \bar{1} & \bar{1} & 1 \\ 0 & 0 & 0 \\ \bar{1} & \bar{1} & 1 \end{pmatrix}^{1/\sqrt{6}}$	$\sigma/\sqrt{6}$	γ	
($\bar{1}\bar{1}$ 1) [011]	$\begin{pmatrix} 0 & 0 & 0 \\ \bar{1} & \bar{1} & 1 \\ \bar{1} & \bar{1} & 1 \end{pmatrix}^{1/\sqrt{6}}$	$\sigma/\sqrt{6}$	γ	$\frac{\gamma}{\sqrt{6}} \begin{pmatrix} \bar{1} & \bar{1} & 1 \\ \bar{1} & \bar{1} & 1 \\ \bar{2} & \bar{2} & 2 \end{pmatrix}$
($\bar{1}\bar{1}$ 1) [1 $\bar{1}$ 0]	$\begin{pmatrix} \bar{1} & \bar{1} & 1 \\ 1 & 1 & \bar{1} \\ 0 & 0 & 0 \end{pmatrix}^{1/\sqrt{6}}$	0	0	

(1 $\bar{1}$ 1) [011]	$\begin{pmatrix} 0 & 0 & 0 \\ 1 & \bar{1} & 1 \\ 1 & \bar{1} & 1 \end{pmatrix}^{1/\sqrt{6}}$	$\sigma/\sqrt{6}$	γ	
(1 $\bar{1}$ 1) [$\bar{1}$ 01]	$\begin{pmatrix} \bar{1} & 1 & \bar{1} \\ 0 & 0 & 0 \\ 1 & \bar{1} & 1 \end{pmatrix}^{1/\sqrt{6}}$	$\sigma/\sqrt{6}$	γ	$\frac{\gamma}{\sqrt{6}} \begin{pmatrix} \bar{1} & 1 & \bar{1} \\ 1 & \bar{1} & 1 \\ 2 & \bar{2} & 2 \end{pmatrix}$
(1 $\bar{1}$ 1) [110]	$\begin{pmatrix} 1 & \bar{1} & 1 \\ 1 & \bar{1} & 1 \\ 0 & 0 & 0 \end{pmatrix}^{1/\sqrt{6}}$	0	0	

$$\sum_{\kappa=1}^{12} e_{ij}^{\kappa} = \frac{\gamma}{\sqrt{6}} \begin{pmatrix} \bar{4} & 0 & 0 \\ 0 & \bar{4} & 0 \\ 0 & 0 & 8 \end{pmatrix}$$

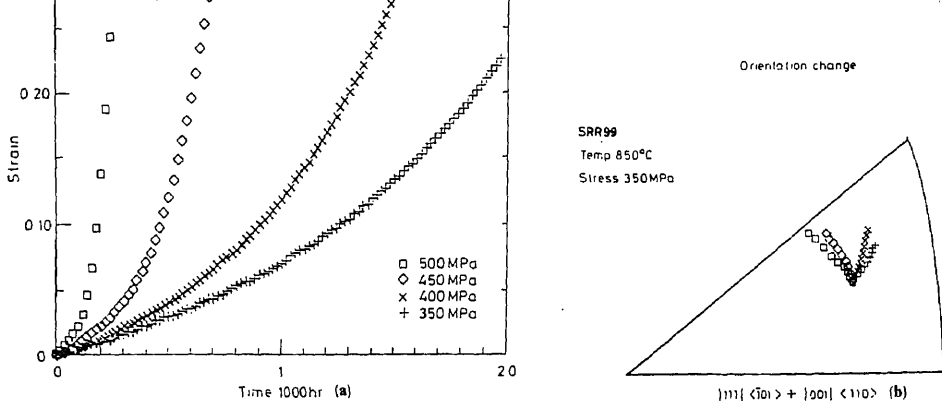


Figure 5. An illustration showing the effect of the applied stress on (a) creep strain accumulation and (b) crystal rotation for SRR99 crystal having $\langle 123 \rangle$ as tensile axis at 850°C .

the likely rotation path if the slip system were either $(111) [\bar{1}01]$ or $(001) [110]$ have been shown. Experimental data reported by McLean *et al* (1992) on SRR99 are shown in figure 4. A comparison with figure 3 will indicate that such a rotation cannot be explained by only octahedral or cube slip. It is indeed more likely that shear deformation takes place simultaneously on both octahedral and cube planes. Using the material constants estimated by Ghosh *et al* (1990) creep curves for $[123]$ crystals have been theoretically calculated at various levels of stress. These have been shown in figure 5a. The likely rotations have been indicated in figure 5b. This shows that the direction of movement of the tensile axis is a function of applied stress. A comparison with the rotation paths indicated in figure 3 would reveal that at low stresses cube slip is more dominant whereas at higher stresses octahedral slip dominates. Therefore a model of creep deformation based on the concept of multiple slip on two types of slip system is capable of describing the observed nature of rotation. Using this concept the performance of SRR99 for all possible orientations can be determined. A summary of such calculations has been presented in figure 6 in the form of a performance map. This shows that at $850^\circ\text{C}/400\text{ MPa}$, $[001]$ crystal exhibits better creep properties, which is quite consistent with experimental data (Ghosh *et al* 1990). Such an exercise clearly illustrates usefulness of a model-based approach for characterizing the creep behaviour of anisotropic material. It can significantly cut down the volume of costly experimental work required to generate such maps. In addition it also suggests simple methods of determining the active slip system by measuring the change in cross-sectional shape of certain crystals of specific orientation. Figure 7a represents the progressive change in the shape of crystal having an initial tensile axis along $[123]$ at a stress where creep deformation is dominated by cube slip; figure 7b represents similar plots to show cross-sectional shape change when slip takes place primarily on octahedral planes. The difference in the predicted shape change clearly demonstrates the influence of slip system on shape change. This method appears to be quite simple and attractive in comparison to direct measurement of crystal orientation using back-reflection Laue X-ray diffraction pattern. Although

h a method could estimate the orientation of crystal prior to testing with an accuracy of 1° , it has proved to be ineffective in case of deformed crystals. Diffraction patterns in these cases are too diffuse to allow meaningful orientations to be determined possibly because of accumulation of dislocations. Experimental data on crystal rotation reported by McLean *et al* (1992) were obtained from an analysis of

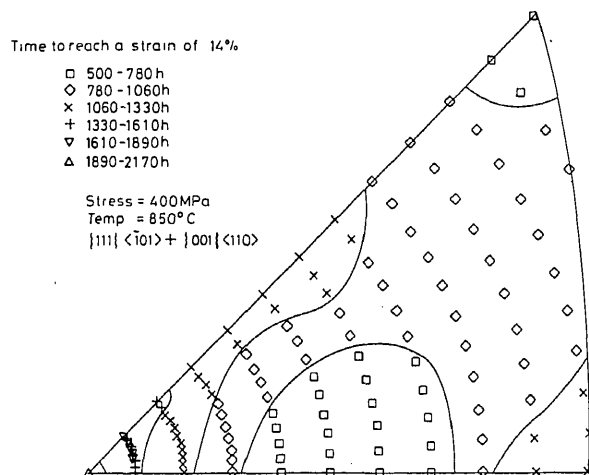


Figure 6. Computed anisotropy of creep performance for SRR99 at 400 MPa/850°C displayed as contours in the unit stereographic triangle as time to reach 14% strain.

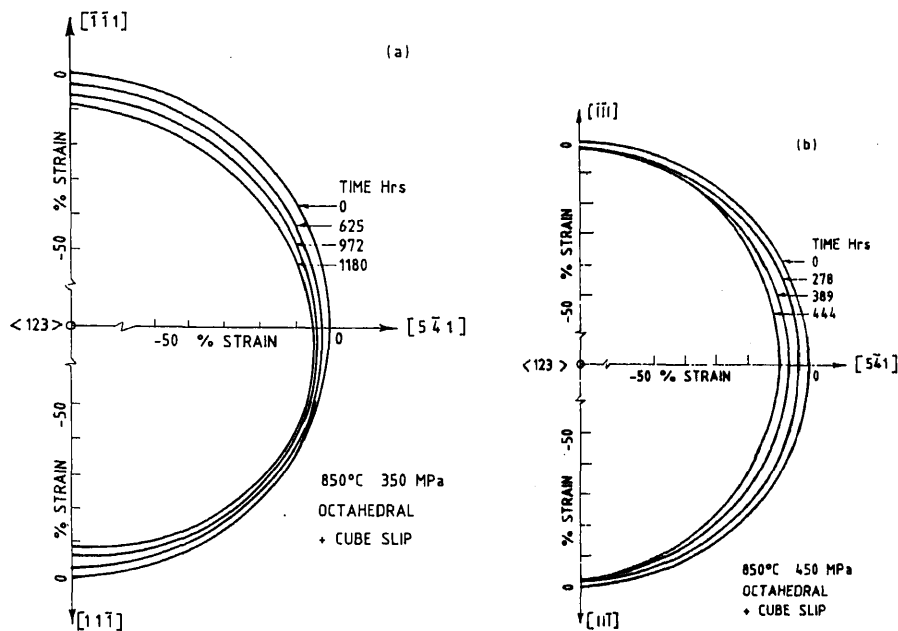


Figure 7. Progressive change in the cross-sectional shape of $\langle 123 \rangle$ crystal at two different stresses: (a) at 350 MPa cube slip is more active, and (b) at 450 MPa octahedral slip is more active.

electron backscatter patterns (EBSP) on a scanning electron microscope. Details of the method are described by Quested *et al* (1988).

Some of the experimental data on shape change reported by McLean *et al* (1992) do indicate that both cube and octahedral planes contribute to creep deformation in SRR99. However, such data are limited. Clearly there is a need to undertake more work in this direction. Nevertheless the present work does suggest a very simple method of establishing the type of operating slip system during creep in superalloys.

4. Conclusions

- (i) A shear stress-based model has been developed for predicting the creep behaviour of a crystal of any arbitrary orientation.
- (ii) Analysis of available data on crystal rotation using the model indicates that both octahedral and cube slips are operative in SRR99.
- (iii) A simple method for identification of the operative slip system has been suggested. This is based on measurement of the change in cross-sectional shape of the specimen.

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Indigenization of high-strength, light-weight Al-Li alloys for aerospace

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Abstract. A research programme was initiated at the Defence Metallurgical Research Laboratory, Hyderabad, a decade ago for the indigenous development of Al-Li alloys in order to finally meet the requirements of the space and aircraft industries in the country. This paper describes the systematic studies carried out in the laboratory to overcome the initial difficulties in producing sound ingots, optimize the subsequent heat treatments and processing schedules, and to finally obtain reproducible microstructure and mechanical properties in the semi products (i.e. sheets and extrusions) developed. Laboratory-scale sheet and extrusion products meet tensile property specification of 8090 alloy. One of these semiproducs, i.e. round bar extrusion, is currently being supplied for the stallite programmes. Commercial-scale sheet products made in Russia under an Indo-Russian joint programme have been made available for the aircraft programme. Recent alloy development studies in the laboratory are discussed within the context of the present paper.

Keywords. Al-Li alloy; ingot casting; heat treatment; mechanical processing; sheet; extrusion; mechanical properties; corrosion.

1. Introduction

Since the recognition of the age-hardening capability of an aluminium alloy containing Cu and Mg in 1906 (Wilm 1911), many complex Al alloys have been developed. Amongst them, Al-Cu-Mg based 2000, Al-Zn-Mg based 7000 and Al-Mg-Si based 6000 series alloys have become very popular. Both 2000 and 7000 series alloys are well known for their use as structural materials for aircraft. In aircraft engineering, there are continuing pressures to develop materials with high specific properties. In the mid 1970s, the changing economics of civilian and military aircraft fleet operation costs, the advent of high-strength, low-density fibre-reinforced composite materials, and in particular of organic matrices with carbon fibre reinforcement accentuated the search efforts for new metallic materials. In metallic systems, one method of achieving superior specific properties is to reduce the density of an alloy while maintaining or increasing the property levels. Reductions in alloy density are more effective than increases in strength or stiffness at reducing aircraft mass (see figure 1). A 10% increase in tensile strength gives approximately 3% mass saving, whereas a 10% decrease in density achieves a 10% mass saving, provided the mechanical properties of the low-density alloy match those of the alloy it replaces (Eknell *et al* 1984). A direct consequence of these practical considerations is that a family of Li-containing Al-based alloys, which were in fact known since the 1950s, reemerged as potential candidates for reexamination and large-scale development.

1.1 Why Al-Li Alloy

Li (having atomic number 3) is the lightest metallic element in the periodic table. Compared to the density of 2.7 g/cm³ of Al, the density of Li is 0.53 g/cm³. As a

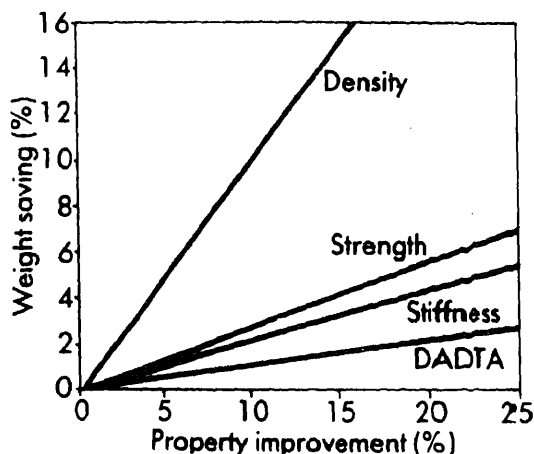


Figure 1. Effect of individual property changes on structural weight savings.

result, Li addition to Al reduces the density by about 3% for each wt% Li added. This is most impressive as weight saving in structure is dominated by a linear relationship with density. Li is an "open" alkali metal (Hume Rothery *et al* 1969). The atomic diameter of Li refers to a relatively compressible structure with a very dilute gas of valency electrons. When Li is dissolved in Al, which is much less compressible, the much stronger bonding forces of Al control the structure to such an extent that the apparent atomic diameter (AAD) value of Li is much smaller than would be expected from Vegard's law (Hume Rothery *et al* 1969). This is the reason why Li addition reduces the lattice parameter of Al, and simultaneously increases the elastic modulus (Mukhopadhyay and Chaturvedi 1989). For a binary alloy containing 2.5 wt% Li, the elastic modulus increases nonlinearly from 66 to 80/82 GPa, the maximum effect on modulus increase being obtained due to the presence of Li in the solid solution in Al (Noble *et al* 1982).

Li is one of the four elements (Zn, Ag, Mg and Li) that have more than 10 at% solid solubility in Al. The maximum solid solubility of Li in Al is about 4 wt% (13.9 at%) at the eutectic temperature of 601°C. Below this, the solid solubility falls rapidly to a low value at room temperature (McAlister 1982). As with the other age-hardenable aluminium alloys, this decrease in solid solubility with decreasing aging temperature provides the basis for strengthening via precipitation hardening by solution treatment and subsequent aging operations. In the case of Al-Li alloys, the major strengthening upon aging heat treatments stems from the widespread uniform precipitation of a metastable coherent phase, δ' , based on Al_3Li (Li_2 structure) (Silcock 1959–1960). Li is therefore unique among the possible alloying elements for Al in that it provides the basis for major precipitation hardening while simultaneously reducing density and increasing modulus.

1.2 Historical development of Al-Li alloy

The attempts to realize the potential benefits of increased modulus and reduced density of Al-Li alloys date back 60 years, although it was not until the 1950s when

Al-Cu-Li AA 2020 was developed in the USA by the Aluminum Company of America (ALCOA). Compared to 7075, which is widely used in the manufacture of aircraft components, AA 2020 has approximately 3% lower density and 7% higher elastic modulus; commercial application of this alloy was made by the US Navy. However, further research revealed that the alloy was notch-sensitive and had a lower fracture toughness than 7075. New US airplane damage tolerance requirements could not be met and the result was the withdrawal of AA 2020 from commercial production, although it continued to be used successfully in existing aircraft. In the USSR, at about the same time, VAD 23, an alloy similar in composition to 2020, was developed. Later, the Soviets investigated and developed a series of Al-Mg-Li alloys referred to as 01420. However, these alloys too exhibited poor ductility and fracture toughness properties. Attempts to improve the mechanical properties were made, but without success. It is now realized that development work was carried out in those days without a proper understanding of the strengthening and deformation mechanisms in Al-Li alloys. In the mid and late 70s, the deformation mechanisms and the principal factors responsible for the brittle behaviour of Al-Li alloys were identified, and the difficulties associated with the casting of high-quality Al-Li ingot were largely overcome. This very substantial progress together with continuing large-scale development programmes inspired Al producers to reexamine and produce more complex Al-Li alloys via both ingot and powder metallurgy routes. In 1983, the British ALCAN International in association with RAE developed, via ingot metallurgy route, the first of the new generation of Al-Li alloys referred to as DTD XXXA (the Aluminum Association code being AA 8090). The DTD XXXA alloy was designed to replace medium-strength 2014-T6 and 2024-T3 plate and sheet in aircraft. In the following years, a higher-strength alloy DTD XXXB was also developed in the UK to substitute for 7000 series Al alloys. Since the introduction of these two alloys, several other Al-Li alloys of varying compositions have been developed by other leading Al producers in the US, France and USSR. The specific weight of these alloys ranges from 2.5 to 2.6 g/cm³ and the elastic modulus from 78 to 81 GPa. This compares with the average values of 2.79 g/cm³ and 71 GPa respectively for the existing aircraft alloys based on Al. It should be pointed out at this stage that during the initial period of Al-Li alloy development, several investigators examined the Al-Li alloy products manufactured by both powder and ingot metallurgy routes. It was realized that the strength-ductility combinations are either equal to or even better in the ingot metallurgy route products than in those obtained via powder metallurgy route. The ingot metallurgy route has therefore been obviously chosen for commercial production of today's Al-Li-based alloys.

Development efforts at DMRL

In the mid 80s, a research programme was initiated at the Defence Metallurgical Research Laboratory (DMRL), Hyderabad, for the indigenous development of Al-Li alloys (via ingot metallurgical route) in order to finally meet the requirements of the defence and aircraft industries in the country. It is the purpose of the present paper to describe the systematic studies carried out at various stages of the continuing Al-Li alloy development programme in the laboratory. Current applications of these alloys, together with recent developments on this alloy type, are also discussed within the

Table 1. Compositions limit for various 8090-type Al–Li alloys.

	Li	Cu	Mg	Zr	Fe	Si
8090	2.2–2.7	1.0–1.6	0.6–1.3	0.04–0.16	< 0.3	< 0.2
DMRL	2.0–2.5	1.0–1.6	0.6–1.3	0.06–0.12	< 0.15	< 0.1
1441	1.6–2.1	1.6–2.1	0.6–1.3	0.04–0.16	< 0.15	< 0.1

context of the present paper. At DMRL, the Al–Li development programme has so far been concerned with mainly the Al–Li–Cu–Mg–Zr-based 8090 alloy (see table 1).

2. Melting, casting and homogenization

2.1 Melting and casting

During the initial stages of the Al–Li alloy development programme, melting and casting of these alloys posed great challenges because the related technologies were not available in the open literature and are mostly proprietary in nature. Melting of Li poses a number of problems due to its high reactivity (Averil *et al* 1981; Divecha and Karmarkar 1981; Starke *et al* 1981). Molten Li reacts with water vapour, oxygen and nitrogen. As a result of its reaction with water vapour, Li oxide forms and hydrogen gets dissolved in the liquid. Dissolved hydrogen can cause microporosity if not removed prior to pouring. Even exposure of molten Li to air during pouring is sufficient to cause oxidation and harm ingot quality. Gas pick-up is accordingly found to be more serious in Al–Li alloys than in conventional Al alloys (Starke *et al* 1981). In order to minimize reaction of Li with the atmosphere, two approaches have been adopted. The first approach consists of covering molten Li by halide fluxes. LiCl and LiF are highly stable compounds and are likely to protect the molten metal (Kamaludeen *et al* 1987). The second approach to minimize Li reaction with the atmosphere is to melt it in an inert atmosphere. Another major problem arising due to Li reactivity is its attack on crucible materials. The attack on crucible materials increases with temperature and concentration of dissolved gases. A low-carbon variety of 304 stainless steel has been reported to give excellent service for Li melting. However, this crucible could not be used for Al melting due to the continual increase in Fe pick-up with time (Chakravorty and Chakraborty 1990). Accordingly, Al and Li have to be melted separately. Two approaches have been adopted in this regard. In one investigation, Li was encapsulated in super-purity Al and then plunged into molten Al with a graphite rod (Jones and Das 1959–60). Another method is to transfer Al melt to Li melt (Chakravorty and Chakraborty 1990).

In DMRL, a twin-crucible melting technique with a combination of flux and argon protection has been developed for the production of up to 50 kg cast ingot (Chakravorty *et al* 1987; Chakravorty 1988; Gokhale *et al* 1988, 1990; Singh *et al* 1989). Special designs were incorporated in the metal mould to minimize melt turbulence and to promote feeding of solidification shrinkage. The argon flushing in the metal mould together with suitable trace-alloy additions are found to improve casting quality. Further studies involving evaluation of the casting characteristics of Li-containing Al alloys showed that these alloys undergo severe metal mould reactions

with sand moulds prepared with sodium silicate binders (Chakravorty and Chakravorty 1991). Alternative mould materials for successful castings have been identified. A high-quality ingot is characterized by its low alkali impurity content, low gas content, low inclusion content, consistent composition, high surface quality, and should necessarily be crack-free. The tendency for hot tearing and porosity formation decreases with reduction in the as-cast grain size. Also, a fine as-cast grain size results in wider distribution of the nonequilibrium solidification products, thus leading to faster dissolution during subsequent processings. Furthermore, in the case of the Al–Li alloys, the final grain structure depends to a great extent on the initial cast structure, since recrystallization in the wrought structure is very difficult to achieve. The latter is partly due to the presence of Zr which is added to control the grain structure during hot working and solution treatment (Ryum 1969; Nes 1972). The grain (albeit the cast grain structure) refining additions of TIBAl has been optimized in this regard. Our studies have shown that 0.4% of TIBAl is required for optimum grain (in the cast structure) refinement (Chakravorty 1988).

2.2 As-cast microstructure and homogenization

Figure 2a shows a light micrograph of a typical as-cast microstructure of an Al–Li–Cu–Mg–Zr-based 8090 alloy produced at DMRL. The micrograph shows that elemental partitioning has occurred during solidification resulting in second-phase precipitation at the boundaries between the grains. Small precipitates observed within the grains formed during cooling of the ingot. SEM studies together with the X-ray mapping of the grain-boundary phases within the as-cast 8090 alloy revealed that the major precipitate at the grain boundary contains Cu and Mg. While Li could

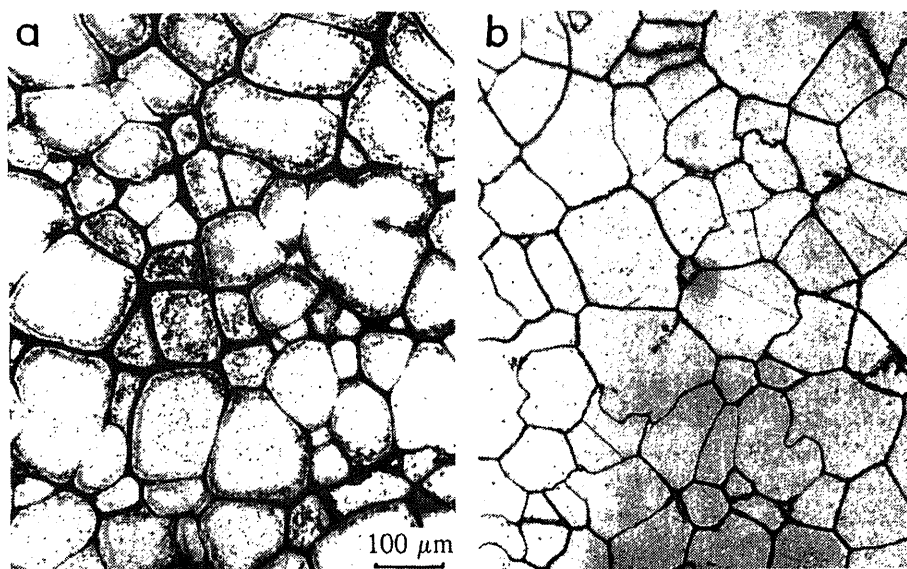


Figure 2. Light micrographs showing (a) interdendritic copper-rich eutectic phases in the as-cast material and (b) homogenized material produced due to annealing at 535°C for 24 h.

not be analysed using X-ray analysis, SIMS analysis of the as-cast 8090 alloys revealed that the Cu, Mg-bearing major grain-boundary phases also contain Li (Mukhopadhyay *et al* 1992). TEM studies conclusively showed that the major coarse g.b. phases are either $T_2(Al_6CuLi_3)$ and/or their approximant variants (Satyaprasad 1990).

With due considerations of the presence of a low-temperature eutectic in the as-cast alloy at about 547°C, the alloy composition, the size of the excess phase particles and that of the dendritic cells in the as-cast structure, an optimum homogenization schedule was determined. Figure 2b shows a light micrograph of the homogenized alloy. It was found that the Fe- and the Si-bearing particles (which separated from the melt early during the solidification) survived the optimum homogenization treatment.

3. Raw materials selection

Deterioration of the strength-ductility combinations as functions of Fe content in Al alloys is a well-known phenomena (Speidel 1975). Presence of a higher amount of Si, i.e. > 0.08 wt%, in Al-Li alloys poses an additional problem by promoting formation of an AlLiSi phase at grain boundaries. The AlLiSi phase survives the optimum homogenization treatment and serves as an active nucleation site for surface pitting upon exposure to salt water and greatly diminishes the resistance of the materials to stress corrosion cracking (Lewis *et al* 1987). The above considerations necessitated using high-purity Al containing 0.08% Fe and 0.07% Si for Al-Li production. Also, alkali impurities such as Na and Ca are also found to result in grain-boundary weakening (Webster 1981). This required further control on raw material impurity contents and processing. Based on the purity requirements projected by DMRL, the National Aluminum Company (NALCO) undertook the development of 99.85% purity Al and has since been able to produce Al to the required purity on a tonnage scale. 99.8% minimum purity Li metal was imported from LITHCO and Cyprus Foote Mineral Company. Other raw materials were available indigenously.

4. Basis for commercial Al-Li alloy composition, and optimum precipitate microstructure

In commercial Al-Li alloys, the major strengthening is due to the precipitation of ordered ($L1_2$ type) and coherent δ' (Al_3Li) phase which forms during or immediately after quenching. The microdeformation characteristics in these alloys are dominated by the interaction of mobile dislocations and the coherent and ordered δ' precipitates. Up to the peakaged condition, such coherent δ' precipitates are sheared by the moving dislocation and planar slip is the result. It has been shown by numerous investigators that such slip coplanarity is the major cause of poor ductility and fracture toughness in these alloys (Sanders and Starke 1982; Noble *et al* 1982; Gregson and Flower 1985). Recent commercial alloys are therefore suitably designed to form semicoherent phases such as $S(Al_2CuMg)$ and/or $T_1(Al_2CuLi)$ in order to disperse coplanar slip leading to slip homogenization in the material. This is the basis for the development of Al-Li-Cu- and Al-Li-Cu-Mg-based alloys. These alloys normally contain trace amounts of Zr to refine grain and to inhibit recrystallization. Zr rather than Cr or

precipitate-free zones (PFZs). These PFZs form near grain boundaries and some equilibrium phases. Studies have shown that the presence of coarse grain-boundary precipitates such as T_2 and δ constitute a major basis for premature grain-boundary failure and low ductility and fracture toughness of these alloys (Vasudevan and Doherty 1987).

Although, as mentioned earlier, planar slip results in low toughness, it can lead to improved fatigue crack growth resistance in three ways. Shearable precipitates promote slip reversibility, cause crack deflections along slip planes, and cause crack branching (Vasudevan *et al* 1984). Accordingly, "Our current understanding of an ideal microstructure for this alloy is the one characterized by the presence of a uniform and fine distribution of both shearable (δ') and non-shearable (such as S) precipitates in the matrix, a reduced width of the PFZs around the grain boundaries, and by the minimal presence of coarse grain boundary precipitates" (Mukhopadhyay and Chakravorty 1993). At DMRL, the 8090 composition was selected as the baseline composition for initial development. The casting quality as well as ductility of the semiproducts were found to decrease with Li content exceeding 2.5 wt%. Therefore, a lower Li content of < 2.5 wt% is used in the alloy production. Similarly, a lower Cu content as well as a higher Mg:Cu ratio (within the 8090 alloy composition) reduce quench sensitivity and coarse g.b. precipitation, and maximize uniform distribution of desirable Al_2CuMg -based S precipitates in the heat-treated microstructure (Mukhopadhyay *et al* 1990b). Details of the alloy design aspects of these alloys have been examined by several workers (Flower and Gregson 1987; Harris *et al* 1987; Mukhopadhyay *et al* 1987b; Sainfort and Dubost 1987; Sanders and Starke 1989).

5. Heat treatment

High-temperature annealing treatments of Al-Li-based alloys, such as homogenization and solution treatments, involve loss of lithium from the surfaces due to oxidation and hence care should be taken to optimize such treatments. For commercial Al-Li-based alloys, the recommended solution treatment temperatures lie in a narrow range, viz. $535 \pm 5^\circ\text{C}$. Solution treatment time, on the other hand, varies from 30 to 90 min depending on the microstructure of the alloy produced due to prior deformation; materials processed at lower temperatures require extended solution treatment in order to solutionize T_2 -type coarse particles which form due to thermal exposure (Mukhopadhyay *et al* 1987a).

Aging heat treatments of alloys of commercial interest involve temperatures lying within the metastable $\alpha + \delta'$ solvus. The maximum aging temperature is always chosen below 200°C . This is because the strengthening falls off sharply when aged above 200°C ; this is attributed in turn to a decrease in δ' (Al_3Li) volume fraction and rapid coarsening of δ' precipitates. Keeping in mind the sluggish precipitation kinetics in Li-containing commercial Al alloys (Flower *et al* 1986, Gregson *et al* 1986), the lower limit of the aging temperature is specified at or above 150°C . The commonly used aging temperature ranges from 150 to 190°C . With increasing aging temperature, the diffusion in the grain-boundary regions is enhanced, leading to rapid grain-boundary

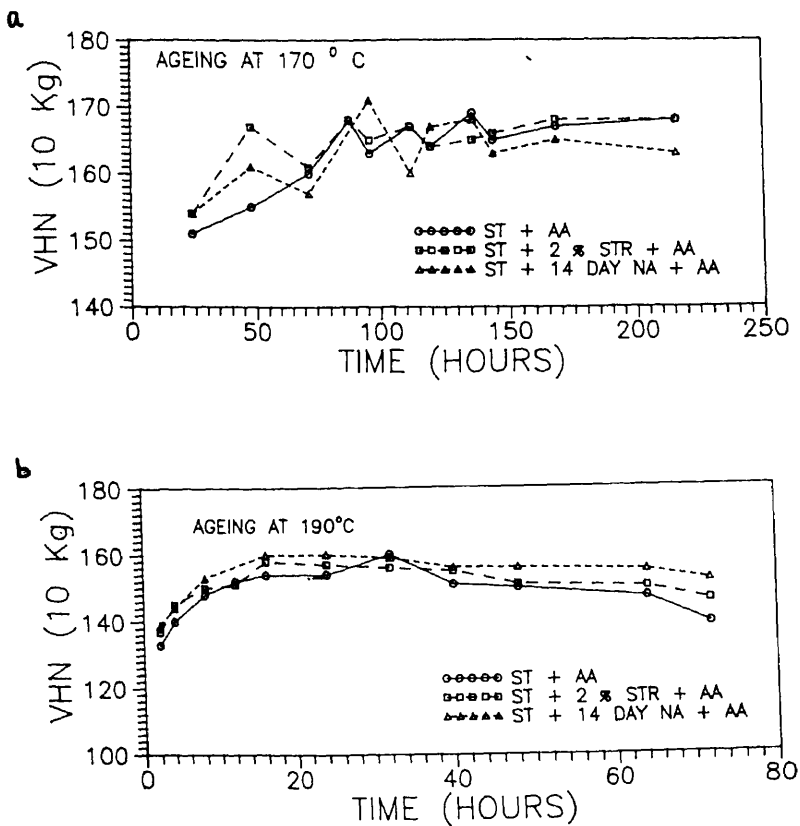


Figure 3. Age hardening curves developed at (a) 170°C and (b) 190°C.

Table 2. Properties of DMRL 8090 sheet products.

Product	Direction	0.2% PS (MPa)	UTS (MPa)	Elong. (%)	Fracture toughness (MPa√m)
Hot rolled sheet	L	404	475	6.0	(L-T):66 (T-L):46
	LT	416	487	7.0	
	45°	377	460	9.1	
Cold rolled sheet	L	370	455	8.5	—
	LT	375	447	8.5	
	45°	354	430	9.5	
Specified	—	360	420	6.0	75

precipitation and formation of the associated PFZs. The present trend is therefore to use a lower aging temperature, combined with prior deformation by stretching (to increase the density of the heterogeneous nucleation sites for precipitation in terms of dislocations), thus attaining the peakaged strength within a shorter time as well as minimizing the extent of grain-boundary precipitation and the associated PFZs (Ashton *et al* 1986).

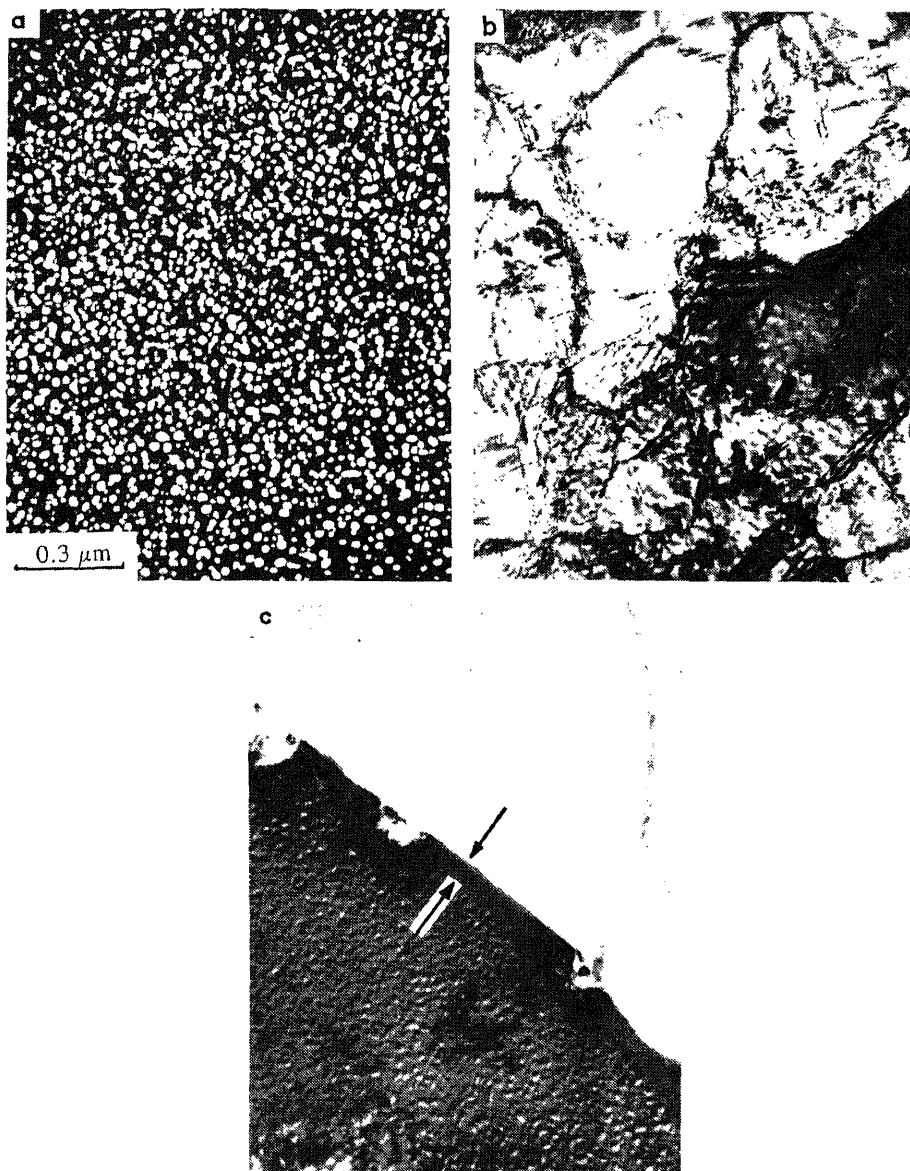


Figure 4. Development of microstructure in the alloy when solution-treated quenched, 2% stretched and aged at 170°C for 24 h: (a) δ' (Al_3Li) phase, (b) S (Al_2CuMg) phase and (c) δ' PFZ adjacent to the grain boundary (arrowed).

Figure 3 shows the age-hardening curves determined for the DMRL alloy at temperatures of 170 and 190°C. It was found that preaging treatments such as 2% stretch or natural aging for 14 days did not change the hardness of the materials appreciably, except during the initial stages of the artificial aging. The 170°C aging produced a maximum hardness. Microstructural studies revealed that the treatment involving a 2% stretch followed by aging at 170°C produced the optimum heat-treated

microstructure (see figure 4). The longitudinal tensile properties of the hot-rolled sheets subjected to different heat treatments (see table 2) support the microstructural analyses.

6. Mechanical processing

Homogenized ingots were scalped to remove the oxidized layers formed on the surfaces and were subsequently processed by rolling or extrusion. Hot-working parameters were first optimized by evaluating the intrinsic workability of the alloys over a wide

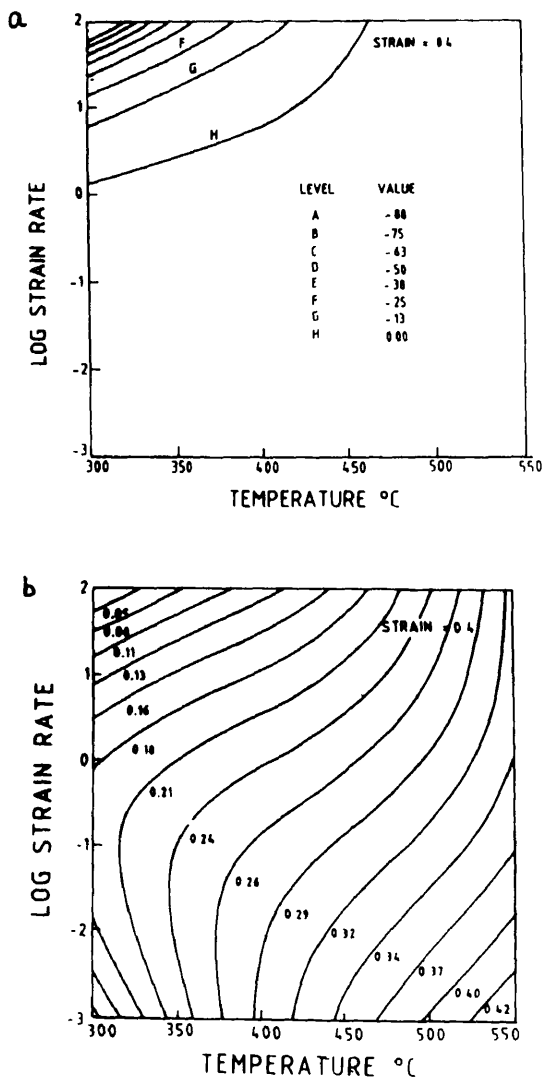


Figure 5. (a) Process stability parameter contour map for DMRL Al-Li cast and homogenized alloy and (b) process efficiency parameter contour map for DMRL Al-Li cast and homogenized alloy.



Figure 6. Light micrograph showing development of grain structure at the mid thickness region of a 4 mm hot-rolled sheet.

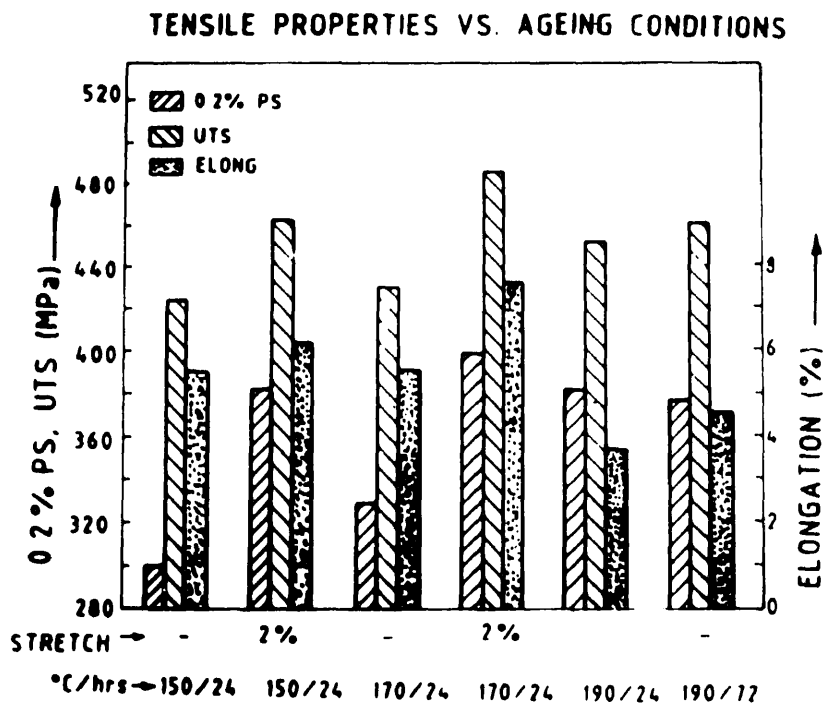


Figure 7. Longitudinal tensile properties of hot-rolled sheets as functions of varying aging treatments.

temperature-strain domain, and then implementing suitable combinations of parameters during extrusion and rolling trials. The intrinsic workability of the alloy was determined from the flow curves from hot-compression tests, and then evaluating the stability and efficiency parameters (Prasad 1990). Figure 5, a and b, shows the stability and efficiency maps for the DMRL as-cast and homogenized alloys respectively (Prasad 1993). Positive stability parameters signify stable and uniform deformation, while higher efficiencies are generally associated with greater degree of recrystallization. Higher temperatures and lower strain rates are found to give uniform deformation and greater degree of recrystallization. Compared to many of the other Al alloys, the rather strong influence of the extrusion temperature on the degree of recrystallization observed in the present 8090 alloys during extrusion is closely related to the dissolution of the coarse T_2 -type precipitates in the microstructure; recrystallization is maximum at temperatures at which these coarse precipitates dissolve (Mukhopadhyay *et al* 1990b).

6.1 Sheets

Sheets of thicknesses 1 to 4 mm were successfully produced. A typical light microstructure of 4 mm (hot-rolled) sheet product is shown in figure 6. The tensile properties of the sheet products evaluated at different orientations with respect to the rolling direction are also presented in figure 7. It is noteworthy that the differences in the property levels between any two of the three directions are small, and that these properties are comparable to the minimum properties specified for aircraft applications.

Fatigue crack growth rates were evaluated in L-T and T-L orientations under constant-amplitude loading as well as LCA spectrum loading conditions. The alloys produced at DMRL were found to have equivalent or lower FCG rates compared to those of 2014 alloy (see figure 8, a and b).

6.2 Extruded products

Rods of 15 to 40 mm and plates of 100×25 and $110 \times 12 \text{ mm}^2$ have been extruded. The as-extruded microstructure revealed that 60% of the peripheral cross-sectional area shows recrystallized grain structure, while the core portion (40%) shows partially recrystallized grain structure (figure 9). The variation in the grain structures observed across the round bar extrudes is also found in the case of many other similarly treated Al alloys. These changes are consistent with the previously documented results on Al-Li alloys suggesting the presence of a strain gradient across the extrude section, where the strain is maximum at the surface and minimum at the core (Mukhopadhyay *et al* 1987, 1990a). Table 3 presents the average tensile properties of the extrudes subjected to the T8 temper. The properties favourably compare with the 8090 minimum property requirements. This product is currently being supplied by DMRL/NFTDC to ISRO Satellite Centre for satellite applications. Table 3 shows that the notch tensile strength values of the DMRL extrusions are comparable to those evaluated from thick plates of commercial Al-Li alloy. Fracture toughness values in C-R orientation of the DMRL extrusions are comparable to those of thick plates of 8090 alloy in L-ST orientation, but inferior to that of 2014 alloy.

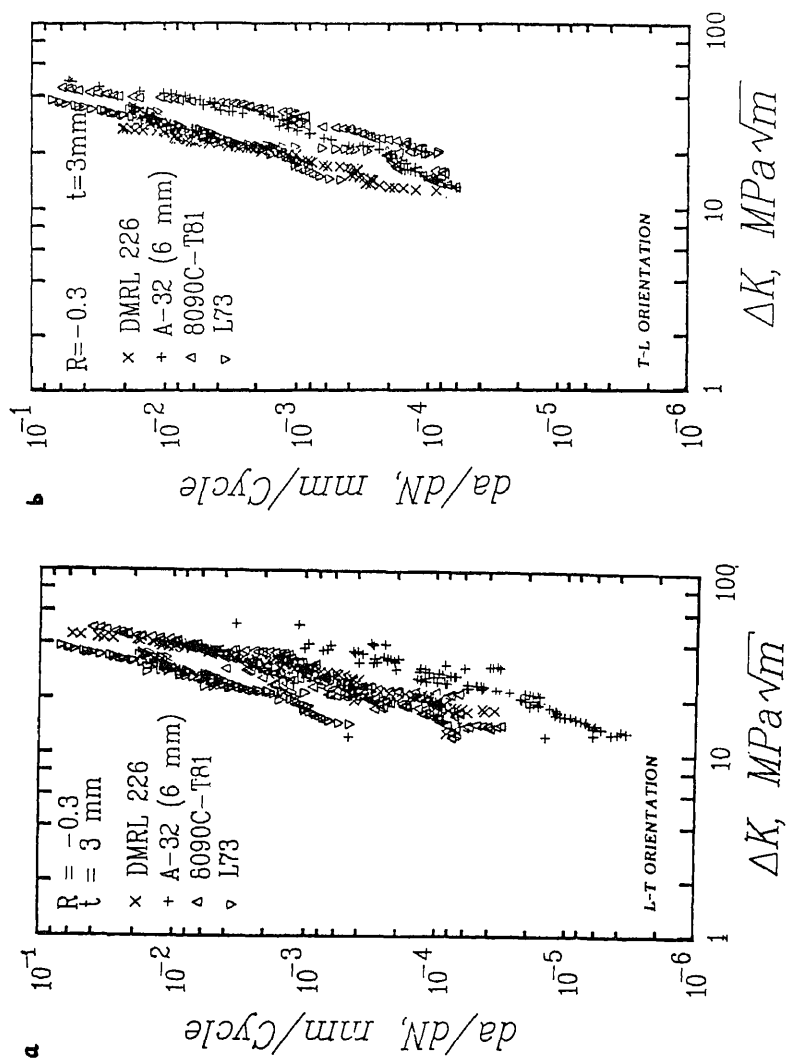


Figure 8. Fatigue crack propagation of DMRL hot-rolled alloy, 3 mm thick, $R = -0.3$, in comparison with 1440 (3-2), L73 (2014) and 8090 C alloys: (a) LT and (b) TL orientation.

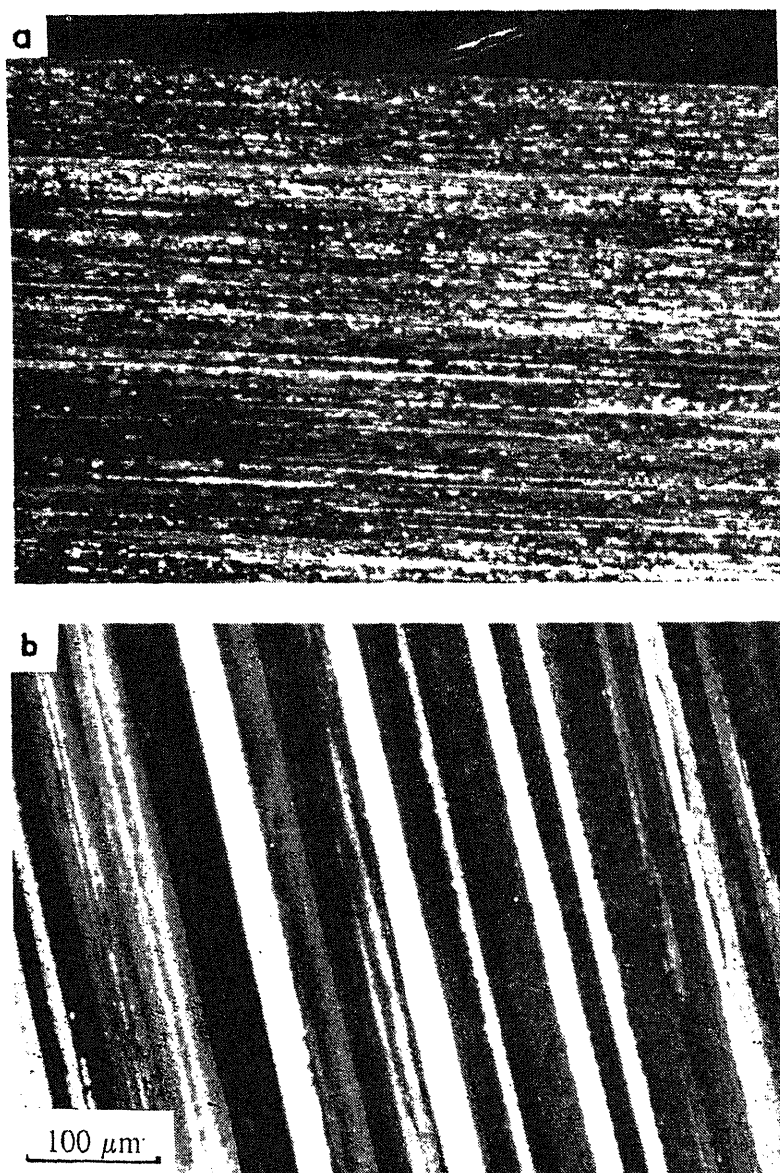


Figure 9. Light micrographs showing variation in grain structure across the extrude section: (a) periphery is fully recrystallized, while (b) the core is unrecrystallized.

7. Commercial-scale production trials

Alloy 1441 was produced in collaboration with NFTDC, Hyderabad, and Russian industries. About 2 tonnes of sheet materials were produced in sizes $1200 \times 3000 \times 1.2 \text{ mm}^3$ (bare and clad), $1200 \times 4000 \times 2 \text{ mm}^3$ (bare and clad) and $1200 \times 4000 \times 8 \text{ mm}^3$ (bare). The tensile properties of the sheet products presented in table 4 are found to be well balanced in different directions with respect to the rolling plane, and also

Table 3. Properties of DMRL 8090 extruded rods.

Alloy	0.2% PS (MPa)	UTS (MPa)	Elong. (%)	NTS	KIC (MPa $\sqrt{\text{m}}$)
				PS	
DMRL	395	465	8.1	1.44	(C-R) 18.9
8090A	380	460	7.0	1.40	(C-R) 10.0
Spec	360	430	4.0	—	—

(Tensile and notch tensile properties in L direction)

Table 4. Tensile properties of 1441 alloys.

Product type	Direction	0.2% PS (MPa)	UTS (MPa)	Elong. (%)
8 mm	L	379	450	9.6
Unclad	LT	375	472	8.9
	450	360	460	6.9
2 mm	L	412	465	8.7
Unclad	LT	389	469	9.7
	450	396	473	9.2
2 mm	L	399	456	9.3
Clad	LT	425	482	8.8
	450	392	461	10.3
1.2 mm	L	401	455	9.7
Unclad	LT	365	445	12.0
	450	375	445	12.3
1.2 mm	L	394	441	9.0
Clad	LT	404	452	8.3
	450	378	430	10.4
Specs		360	420	6.0

compare favourably with the specified property requirements. Fatigue properties have also been evaluated extensively and are found to be largely independent of test orientation and sheet thickness. Cladding is found to increase the fatigue crack growth rate by a small extent (Saxena 1993). This result is consistent with the previously documented results on smooth specimen fatigue behaviour (S-N curve) (Polmear 1989).

8. Work in progress and future plans

The alloys are being evaluated for corrosion properties at DMRL as well as in collaboration with BE college, Shibpur; IIT, Kanpur; and DMSRDE, Kanpur. Initial work indicates that the exfoliation corrosion resistance of DMRL Al-Li alloys is superior to that of 2014 alloy (Banerjee 1993), and that it is dependent on the degree

of aging with the underaged alloys being immune to exfoliation corrosion (Tripathi 1993). Recent studies have shown that the rate of corrosion of DMRL alloys in corrosive media (such as 3.5% NaCl solution) is markedly reduced in the presence of trace additions of Zn (Singh *et al* 1994). Work involving development of 8090 alloys having combination of higher strength, toughness and stress corrosion cracking (SCC) resistance are in progress (Singh *et al* 1994).

Plans to scale up the melting and casting process are in progress.

9. Summary

Laboratory-scale Al–Li–Cu–Mg-based 8090 alloy semiproducts have been developed with microstructure and tensile properties comparable to those of commercial Al–Li alloys. One of the semiproducts, i.e. extruded rod products, are being supplied to ISRO for the space programmes. Alloys having improved combinations of strength, toughness, and corrosion and stress corrosion cracking resistance properties are being developed. Scale-up of the existing production technology is in progress.

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Challenge, response and serendipity in the design of materials

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Abstract. A number of condensed case-histories of successful materials innovations are presented to illustrate the author's thesis that happy accident favouring the prepared mind (i.e. serendipity), or alternatively a response to a challenge from competing materials, are circumstances favouring effective innovation.

Keywords. Case histories; age-hardening; transformer laminations; lamp filaments; nanostructures and nanofilters; superalloys; strong fibres.

1. Introduction

The British historian Arnold Toynbee, in his ambitious multivolume *History of the World*, introduced the concept of 'challenge and response', the notion that throughout history, one nation, one class, one religion, one army, challenged another and was met, usually, by a forceful response to the challenge. In this way, empires, civilizations, religions and dominant classes alternated, according as the challenge or the response prevailed. The same thing has happened, in a less dramatic form, in the development of new materials. One family of materials (for instance, silicon-iron in transformer laminations) had the market to itself for a long time, and nothing much changed for many years; then a challenger came with better properties (here, metallic glass) and the makers of the dominant material responded in panic by improving their ancient product in a hurry. The response would not have happened without the challenge.

But not all innovations are determined by this kind of 'force of arms': accident plays its part in this process, as it does in all aspects of human life. As we know, 'accident favours the prepared mind', and if accident, mental preparedness and sheer good luck come happily together, what we get is serendipity. This curious word derives from the legendary Prince Serendip of old Ceylon, who always had flawless good luck (that is why he was legendary). Serendipity requires good luck, but that is never enough: the innovator must be able to recognize what is staring him in the face, and that in turn requires years of experience, plus open-mindedness. Many important materials innovations stem from sheer serendipity. I outlined some of these a few years ago in another Indian publication (Cahn 1981).

2. Serendipity

2.1 Age-hardening

Age-hardening was discovered, as every student of metallurgy learns in his first undergraduate year, by Alfred Wilm, the head of a newly established metallurgical section in a German government research institute near Berlin in 1906 (though in the leisurely manner of those days, he did not publish his findings for another five

years after that). In the course of a wholly empirical search for strong aluminium alloys, he was examining an alloy containing 4 wt% of Cu, 0.5 wt% of Mg and 0.5 wt% of Mn, in the cast-and-rolled condition (later it came to be called 'duralumin'). He examined its indentation hardness on a Saturday, went off for a leisurely weekend (yes, metallurgists had leisure in those far-off days) and on returning next Monday, he repeated his measurements, just to be sure. The alloy was now 40% harder than before. Wilm knew better than to shrug off this finding as a result of mere careless measurement. He repeated the experiment properly and determined the first age-hardening isotherm. By 1914, duralumin was being used to build airships to bombard the British enemy.

This discovery was clearly serendipitous, but not sufficiently so, because there was no basis available for finding any other age-hardening alloys. The Harvard metallurgist Albert Sauveur reported to the US Air Service in 1918 that he did not know of any other metal or alloy exhibiting a similar phenomenon, so that analogy did not help. Thereupon, in 1919, Paul Merica, a metallurgist at the National Bureau of Standards in Washington, studied the solubility of copper (Wilm's predominant solute) in aluminium as a function of temperature, using simple optical micrography, and found that the solubility increased sharply with rising temperature (Merica *et al* 1920). The secret of age-hardening was now manifest: it clearly depended upon the precipitation of the equilibrium phase from a supersaturated solid solution (in duralumin this happens slowly at room temperature, highly surprising in itself). Of course, like all confident generalizations, this one was only partly true: in fact, it is a metastable precursor of the stable phase, CuAl_2 , that achieves the hardening, and by the time the stable phase forms, it is all over. Also, we now know that much of the hardening in this particular alloy comes from the precursor of the Mg_2Si phase rather than from CuAl_2 ; the Si here was an unintended and unsuspected impurity. No matter, once it was known that an increasing solubility with rising temperature was the key, a simple inspection of phase diagrams, or a few days' work to establish the relevant part of a new phase diagram, sufficed to point the finger at new potential age-hardening systems. Serendipitous observation always needs to be supplemented by systematic investigation.

Wilm's original paper of 1911 appears in translation in an excellent little book by Martin (1968).

2.2 *Electric light filaments*

When Edison invented the incandescent electric lamp, he was plagued by endless difficulties with his filaments; he began with charred organic material and never managed to produce an effective metallic filament. That achievement fell to William Coolidge, the legendary metallurgist who eventually directed the General Electric Research Laboratory in Schenectady, NY (he also gave his name to the modern type of X-ray tube). In 1913 Coolidge took out a US patent on ductile tungsten, made by powder metallurgy, which allowed ultrafine filaments to be drawn down from a metal rod. For such filaments to be useful, they had to have a long life. Two features were noted to limit this life: one was evaporation from the tungsten to deposit on the lamp envelope, which soon became opaque (even before the tungsten all evaporated away), the other was the white-hot filament slipping apart along grain boundaries. Irving

Langmuir, the Nobel-prize-winning physical chemist who was Coolidge's most distinguished colleague, cured the first problem by filling the lamp with a noble gas. The second problem was far more difficult, and Coolidge solved it by a classic exercise in serendipity. He noted that tungsten powder annealed in one particular make of crucible, imported from Germany, after sintering and drawing down did not have the grain-boundary problem, and micrographic examination showed that in this batch, the grain boundaries were all longitudinal: this proved to be the essential microstructure that conferred long life on the filaments. Next, Coolidge followed up his lucky accident with systematic work: the successful tungsten powder was analysed and found to contain potassium and aluminium silicate, picked up from the refractory. Thereafter, small amounts of these 'dopants' were added intentionally to the tungsten powder (with a shovel, on the shop floor); this is still done today (to the tungsten oxide precursor), even if a shovel is no longer used! The long-lived Coolidge, who became a centenarian, described his inspired innovation in a historical book published in 1965 (Coolidge 1965), but he still did not know, 52 years later, why his dopant worked so well. It was discovered subsequently, by TEM, that the dopant produces microbubbles of potassium vapour during sintering and the drawing process draws these out into strings which act to constrain migration of the grain boundaries and thus to achieve the required microstructure. The three doping constituents were needed to generate a fairly stable compound which only releases potassium vapour at a late stage in sintering, when porosity has become closed. Here, as so often in the history of materials technology, the scientific explanation came long after successful practice was established. The historical stages, of both the technology and the science of tungsten lamp filaments, have been very clearly outlined by Welsch and Walter (1990).

2.3 *The beginnings of superalloys*

The development of the gas turbine, to power a jet engine, began independently in England and Germany at the end of the 1930s; from an early stage it had become clear that an utterly novel type of alloy would be required for the turbine blades and disc and this led to a crash programme of alloy development, of what came to be called 'superalloys'. The English side of this programme has been described by one of the chief protagonists, L B Pfeil (Pfeil 1963), and an outline of this work and of the slightly later stages of superalloy improvement has been presented in a more accessible publication by Cahn (1973).

Like the discovery of age-hardening and of ductile sintered tungsten, superalloy development began with a happy accident, acutely observed by a 'prepared mind'. Development had begun with tests of 80/20 nichrome, long used for the filaments of domestic electric heaters. Different batches did not behave consistently and the best behaviour was traced to batches which had been contaminated with titanium and a little carbon, because of deoxidation of the melt with titanium (not a universal practice). Thereupon the titanium content was intentionally increased and further improvement in properties resulted. There were still surprising variations and at this stage a little science was injected, in the form of the determination of some partial ternary phase diagrams. A working hypothesis was now formulated, that of 'marginal solubility': the idea was that the best creep resistance required alloys with just more of each solute than was soluble at the service temperature; this idea arose because

it had become clear that effective age-hardening alone was not enough to guarantee good creep resistance. That working hypothesis proved to be rather too simple, but meanwhile it served as an 'energizer'. This often happens in materials research as it does in ordinary human life: a false hypothesis leads to action which eventually reveals a better hypothesis. Another accident based on a false hypothesis led to the introduction of aluminium into superalloys, probably the most important improvement of all. That in turn led Taylor and Floyd (1951-52) to one of the great classics of phase diagram research, on the Ni-Al-Ti system, in which they were able to show that $\text{Ni}_3(\text{Al}, \text{Ti})$ was the crucial precipitating phase. Hereafter, development became ever more science-based, with studies of lattice parameter misfit between the ordered and disordered phases as a function of alloying strategy and of the factors, including small misfit, that so effectively stabilize the ordered $\text{Ni}_3(\text{Al}, \text{Ti})$ dispersion against Ostwald ripening. These stages, leading to the successive members of the famous NIMONIC series of superalloys manufactured in England, are described in Cahn's overview (Cahn 1973).

A recent, systematic survey of superalloys (Tien and Caulfield 1989) fails to mention any aspect of the early development and presents superalloys as though they were an exclusively science-based success story; but then this volume is fixated on the American end of the superalloy story and the name 'NIMONIC' never appears in the book! Generally, many scientists are shy about citing any reference more than ten years old lest they be thought out of date and (worse) backward-looking; but by this omission, they fail to learn from history.

2.4 Nanofilters

In 1967 the second major report from the US National Academy of Sciences to the US House of Representatives, following a formal agreement between the two bodies in 1963, was published in Washington (Committee on Science and Public Policy 1967). This was entitled *Applied Science and Technological Progress*, and it was the first of several memorable reports of this kind with a close bearing on materials. This report, which is very little known and was hard to obtain even at the time, deserves renewed attention, maybe even republication. It includes, among many other items worth reading, a splendid historical overview by Cyril Stanley Smith and thought-provoking essays by people like Harvey Brooks, Edward Teller, Alvin Weinberg and others. However, from my present perspective, the key chapter is one by C Guy Suits and Arthur M Bueche, both past directors of research at General Electric in Schenectady, NY. Their title is 'Cases of research and development in a diversified company'.

The fascinating chapter records in detail the history of 10 innovations, most of them concerned with materials, and then goes on to draw a number of broad conclusions about the sources and uses of applied research and about the role of patents. Each record starts with a narrative account of the sequence of events and concludes with a list of key personnel (with a few words about each individual), a list of patents issued and of some key publications. GE has for many years employed a professional historian on its staff, and his influence is clearly visible in the chapter; it would be a fine thing if more major companies followed this policy. (Elsewhere, I have tried to place this practice of recording case histories of innovation in a broader

diamond and is typically referred to as 'synthetic' and use a vacuum circuit breaker (a major industrial product) which turned out to depend entirely on the use of zone-refined copper to eliminate degassing of the electrodes in their permanently sealed vacuum enclosure. This crucial innovation took some 40 years to reach a successful conclusion and incidentally represents the only recorded useful application of zone-refined metals, as opposed to semiconductors. Yet another very major innovation described here in some detail was the creation of a large new industry, the production of high temperature vapour lamps, with translucent alumina envelopes (glass or silica were useless), all springing from some fundamental research on the mechanism of sintering of alumina powder. This again was a classic example of serendipity, arising out of a chance encounter between ceramic researchers and a lamp engineer.

However, the most extraordinary episode recorded in the chapter refers to 'etched particle tracks'. The work in question was undertaken in the 1960s by three well-known physicists on the GE staff, R M Walker, P B Price and R I Fleischer. Suits and Bueche raise the question of why such very 'pure' research should be undertaken in an industrial laboratory. Part of their answer is: '...experience has shown repeatedly that studies begun solely to grapple with fundamental questions of science can be rewarding to industrial technology, *providing advances for which there was no pre-existent need* [my italics], however strong that "need" might become afterwards'. I wonder how many research directors would dare say this today! The original objective was to develop and study cosmic ray-tracks in meteorites, and thereby develop a new method of geological and cosmological dating; in this it was successful. Part of the research involved the creation of artificial tracks, by shooting fission fragments from uranium through thin slivers of mica and 'developing' the tracks chemically. As a sideline, the investigators exploited their finding that an irradiated and etched mica sliver contained minute, submicron holes all exactly the same size. By word of mouth this work came to the ears of a cancer researcher in New York, who needed to isolate and detect cancer cells in blood by filtering the blood through sieves that would hold back the larger, more rigid cancer cells while allowing smaller cells to pass through. Fleischer thereupon sought materials less fragile than mica to use for making such sieves, and found that GE's own patented polymer, LexanTM polycarbonate, served very well. The upshot was the creation of a small but lucrative industry manufacturing NucleporeTM filters for biomedical research; this manufacture is still in existence and has broadened into several companies. This is one of the most convincing instances of serendipity known to me.

2.5 Ashless polymers

The commercially trained eye can often see possibilities that would never occur to the cloistered academic. A good instance of this comes from a small company in Pennsylvania. J U Santangelo in this company exploited chemical researches done in Japan in the mid 1960s on copolymerization of epoxies with carbon dioxide to produce commercially a family of polymers consisting about 50% of CO₂; these are generically named poly(alkylene carbonates) (Santangelo and Tao 1990).

Thermogravimetric analysis of such polymers (a normal investigative technique to check on thermal stability) showed that they decompose and burn cleanly at around 240°C. What was unusual, and perhaps to be expected in materials containing so much CO₂, was that the material left virtually no ash at all, less than 2 ppm. Accordingly, Santangelo is offering this product as an ashless binder for ceramic and metal powders that are to be sintered, and as a substitute for expanded polystyrene in lost-foam casting.

The foregoing examples indicate what a wide variety of innovations have resulted from serendipitous observations.

3. Challenge and response

3.1 Transformer laminations

In 1899, Barrett and Hadfield in England stumbled upon the fact that silicon-iron containing 3–3.5 wt% of silicon shows low hysteresis when magnetized, and is also easy to process because the silicon suppresses the ferrite–austenite transformation. Ever since, silicon-iron sheets, coated with insulator to reduce eddy currents, have been used to make transformer laminations. It is a very large industry indeed, worldwide.

The magnetic characteristics of silicon-iron strip were further improved when Goss found how to generate a (110)[001] texture by secondary recrystallization, which was beneficial because of the anisotropy of permeability in iron crystals. Between 1968 and 1977 various companies in Japan and the USA found ways of sharpening the texture, thereby achieving some further improvements in magnetic performance (Luborsky *et al* 1983); this work was clearly stimulated by normal commercial competition between rival manufacturers.

Enter, stage left, the challenger. In 1958, Pol Duwez in California, with his collaborators, discovered the first melt-quenched metallic glass in the Au–Si system (see historical overview by Cahn (1993)), and the same year Gubanov in Russia first suggested that a metallic glass should be capable of having ferromagnetic properties, an idea which had not occurred to anyone previously. This was soon confirmed experimentally with iron- and cobalt-rich glasses. There was a gap of some years before this idea was followed up, but from the beginning of the 1970s research gathered pace and in 1973 the first multiauthor volume on ‘Amorphous Magnetism’ was published. By the beginning of the 1980s, the subject had become firmly established, with numerous research teams across the world. Furthermore, several manufacturers had begun to produce sheets of ‘soft’ ferromagnetic glasses with high permeability and low coercive field, up to a foot or so in width, using ingenious developments in rapid solidification technology; one American firm was particularly aggressive in this field. It was striking that three distinct research teams independently optimized the composition of such glass for transformer uses and came up with virtually identical compositions based on Fe–Si–B with, sometimes, a little carbon. Such glasses have the following advantages over silicon-iron: no appreciable intrinsic anisotropy of permeability (although a favourable anisotropy can be induced by field-annealing), very low intrinsic magnetic losses, a high electrical resistivity which reduces in-plane eddy current losses. A disadvantage is the fact that the saturation magnetization is somewhat lower than in crystalline alloys. Overall, the core loss in

metallic glass laminations was found to be an order of magnitude lower than for 3 wt% silicon-iron.

At this point, the transformer manufacturers began showing serious interest, especially in the US and Japan in connection with 'distribution transformers', which are located near individual consumers to transform voltage down to 110 V (this market does not exist in Europe). Such transformers are small enough to utilize the glass sheet with its limited width, and enormous numbers are required every year. The Electric Power Research Institute in California commissioned a large-scale industrial trial of metallic glasses in these products.

Starting from about 1980, the steelmakers read the writing on the wall, and began to fight back. The first approach was to try to increase the silicon content in (crystalline) silicon-iron, thereby enhancing the resistivity and thus reducing eddy currents. Ironically, to achieve this the steelmakers exploited the same technique which made metallic glasses possible, namely rapid solidification processing (RSP). Up till then, 3.5 wt% was the practical limit of silicon concentration, since any more than this led to great brittleness so that the alloy could not be rolled into sheet. RSP allowed ductile silicon-iron to be made with up to 6.5 wt% of silicon. Usually this was without texture (a weakness), but with elaborate processing involving several rollings and anneals, an ideal (100)[001] texture could be achieved, albeit at considerable cost (e.g. Kan *et al* 1982). In 1982, the commercial price of metallic glass sheet was still about 10 times that of the cheapest oriented iron-silicon sheet, so the steelmakers' alarm might have seemed premature. However, as shown by Smith (1993), by 1990 the price differential had disappeared, as indeed the glass manufacturers had predicted six years previously. It seemed that the 3.5 → 6.5% solute shift was not enough to fight off the challenge (although Smith suggests that the enriched silicon-irons may have a rosy future in electric motor laminations, where price is considerably more important than performance).

In the late 1980s, accordingly, the steelmakers (especially those in Japan) became more sophisticated. A good example can be seen in a paper by Inokuti *et al* (1992), entitled 'Grain-oriented silicon steel sheet with new ceramic films characterized by ultra-low iron loss'. This work refers to commercial 3.3 wt% silicon-iron with the usual Goss texture. The sheet was chemically polished and then either CrN or TiC was ion-plated (physically deposited with a hollow cathode discharge) on the sheet while that was held under tension. The result was that the surface layers of the sheet were under strong tension and this led to a sharply reduced stress dependence of magnetostriction and in turn to a 40% reduction in core loss. Coatings to enhance surface stress have long been used, but this approach takes the technique to a new level of sophistication. Nothing is said about commercial costs, so one cannot judge how this approach changes the commercial balance sheet! The battle continues.

3.2 Strong fibres

Fibre-reinforced composites with polymeric, metallic or ceramic matrices are being improved constantly; both strength and temperature capability are constantly being enhanced. The variety of reinforcing fibres available now in the market constitute a prime illustration of challenge and response. The rivals include crystal whiskers (the strongest and the most expensive), ultrafine metal wires, including so-called Taylor wires; glass fibres; boron fibres, usually on a tungsten core; silicon carbide fibres made

by several distinct processes; carbon fibres, ditto; alumina fibres; and a variety of strong polymeric fibres, notably Kevlar and polyethylene.

Historically, glass fibres for reinforcing cheap epoxy polymers came first, and they continue to hold the less expensive end of the market; the strong polymeric fibres were a response to the dominance of glass, which in turn was improved by composition changes to stand up to the chemical environment of a cement matrix (the cheapest of all). Whiskers (never more than 1–2 mm in length) created great interest because of their exotic manner of production, but in spite of recurrent flickers of life, they cannot really compete anymore with modern continuous fibres. Carbon fibres made from a polyacrylonitrile precursor started in Japan and were soon perfected in Britain, and increasingly hold the expensive end of the low-temperature market. Later, a challenge came from Japan, where in 1975 Yajima was able to make SiC fibres from a polymeric precursor; it took a long time for these to make inroads in the market, and he became so discouraged that he took his own life. But soon after, his fibres became a commercial success and hold a special place for high-temperature uses. Boron and alumina fibres are even more expensive but are beginning to make inroads in defence uses where cost is secondary. The commercial balance remains uncertain and battle continues.

An early brief critical discussion of alternative fibres came in a special issue of the journal *Materials Science and Engineering* devoted to 'Challenges and opportunities in materials science and engineering'; the authors were Chou and Kelly (1976). Later, Kelly (1986) critically discussed the modes of manufacture, merits and weaknesses of rival reinforcing fibres and wires in his standard text, while a more recent comparison comes in a new volume on composites (Parvizi-Majidi 1993).

3.3 Nanostructured WC-Co 'hard metals'

Nanostructured materials have been the subject of very rapidly increasing research for some seven years now, and in 1991 they achieved the status symbol of their own dedicated journal. I surveyed the early stages in the progress of this impressive bandwagon in 1988 and 1990; these articles have recently been reprinted (Cahn 1992). One of the first proper commercial applications of these materials with submicron-scale microstructures refers to the familiar long-established 'hard metal', widely used for making metal-cutting tools particularly; they consist of hard, brittle tungsten carbide crystals dispersed in a softer, ductile cobalt matrix. This material is facing increasing competition from rivals such as sialon, oxides and indeed diamond layers deposited by CVD: there was thus a good marketing reason for aiming at some kind of major improvement in hard metal.

Kear and McCandlish of Rutgers University in New Jersey have developed such an improvement in the past four years, and have reported on it in a new journal (Kear and McCandlish 1993). Normally, a hard metal block is made by co-sintering (and perhaps hot isostatically pressing) a mixture of WC and Co powders, and the microstructure is quite coarse. Kear and McCandlish learnt from chemical engineering practice and started from an organometallic precursor, cobalt tris(ethylenediamine) tungstate, which after spray-drying and then thermochemical conversion in a fluid bed reactor gave WC-23 wt%Co powder. Careful control of gas composition and temperature to achieve rapid and controllable carburization was an essential component

of the process. The incorporation of some VC to inhibit grain growth was found essential. In this way, a very fine-structured product can be made, and this, as expected, resisted cracking to much higher stresses than the conventional product. This in turn allows faster machining when the new product is used for cutting tools. Kear and McCandlish opine that their 'spray conversion processing' has much unrealized potential for producing other flaw-free, nanostructured materials also.

4. Conclusions

These few instances of my two categories of innovative materials could be multiplied manifold. Some are at an early stage, such as systematic design of advanced steels from first principles or the production of diamond films from the vapour phase, others are further developed, such as magneto-optical memories for computers.

I would leave the reader with one thought. Too few academic groups and indeed industrial companies keep detailed records of the kind that would permit systematic historical accounts of the genesis, growth and maturity of a new product to be assembled, in the way that GE was able to do in the 1960's. The whole research and development community has much to learn from such accounts: perhaps there is a case to be made for government financing of such innovative histories, and perhaps of comparative studies of success and failure of innovation. As recorded in my 1970 paper (Cahn 1970), in the 1960s there were many such studies; perhaps today we are too surfeited with a mass of information to cope with. But it is precisely at such a time that reviews, surveys and concise histories are particularly valuable. Perhaps it is time to start again.

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Growth of diamond thin films by chemical vapour deposition

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Abstract. Deposition of diamond thin films on non-diamond substrates at low pressures (< 760 torr) and low temperatures ($< 2000^\circ\text{C}$) by chemical vapour deposition (CVD) has been the subject of intense research in the last few years. The structural and the electrical properties of CVD diamond films grown on p-type $\langle 111 \rangle$ and high-resistivity ($> 100 \text{ k}\Omega\text{-cm}$) $\langle 100 \rangle$ oriented silicon substrates by hot filament chemical vapour deposition technique are described in this review paper.

Keywords. Diamond; thin films; chemical vapour deposition; Raman spectroscopy; sheet resistivity.

1. Introduction

Exceptional properties of diamond have attracted the attention of the research community throughout the world to exploit these properties for a variety of applications ranging from hard coatings for drill bits to high-temperature electronics. The ability to grow thin films of diamond using inexpensive chemical vapour deposition (CVD) techniques has led to intense research on the characterization of these films in the last few years (Angus and Hayman 1988; Yarbrough and Messier 1990; Davis 1993). Several methods for diamond deposition on non-diamond substrates with high deposition rates ($10\text{--}300 \mu\text{m/h}$) have been described (Matsumoto *et al* 1982). The crystals grown from these processes were many micrometres in size and were often twinned and without preferred orientation relative to the substrate. Process variables such as methane concentration, substrate temperature, system pressure and flow rates of methane and hydrogen are varied to control the quality, composition, grain size, surface texture and growth rate of the films (Mercier *et al* 1991; Zhu *et al* 1991). The use of atomic hydrogen for removing co-deposited graphite (stable phase of carbon at room temperature and pressure) to result in metastable growth of diamond has been well established. The nucleation of diamond particles on non-diamond substrates has been studied extensively (Kobashi *et al* 1989; Meilunas *et al* 1989). However, no clear understanding of the nucleation process has emerged.

2. Fabrication

2.1 Different kinds of CVD methods

During the past decade, different CVD methods have been employed to grow high-quality diamond thin films on a variety of substrates. The common features of all these methods are: (1) high energy densities to produce hydrocarbon species in the gas phase, (2) high substrate temperatures ($600\text{--}1000^\circ\text{C}$) to ensure diffusion of the species on the substrate surface to enhance nucleation, and (3) efficient utilization of

atomic hydrogen to result in the etching of graphite. The fundamental difference in these methods is the way the chemical precursors are activated by different types of energies. The major CVD techniques are: (i) hot filament CVD and (ii) microwave plasma enhanced CVD, (iii) r.f. plasma enhanced CVD (Davis 1993). Microwave plasma enhanced CVD appears to be the most common growth technique. This method uses 2.45 GHz microwave power as the source to dissociate the reactant gases. Highly oriented diamond films have been fabricated by this method (Stoner *et al* 1992). The hot filament CVD technique used in our work is described in detail below.

2.2 Hot filament CVD system

This is the most simple and economical diamond growth technique. As shown in figure 1 a tungsten filament is heated to about 2000°C to dissociate the hydrocarbon-hydrogen gas mixture during the growth process. As seen in figure 1, the reactant gases, i.e. H_2 and CH_4 , are introduced from the top into the reaction chamber. The amount of the reactant gases is controlled by a Dyna Mass flow control system. The silicon substrates are placed on a molybdenum substrate holder and are held by molybdenum fingers. The substrates are heated by a tungsten coil placed underneath the substrate holder to independently control the substrate temperature. A type K thermocouple (Ni-Cr/Ni-Al) that is placed firmly in contact with the bottom of the substrate holder measures the substrate temperature. The temperature of the tungsten filament maintained close to 2000°C is sensed by an Omega two-colour (model OS 3722) optical pyrometer which can measure temperatures from 900 to 3000°C with an accuracy of $\pm 1\%$.

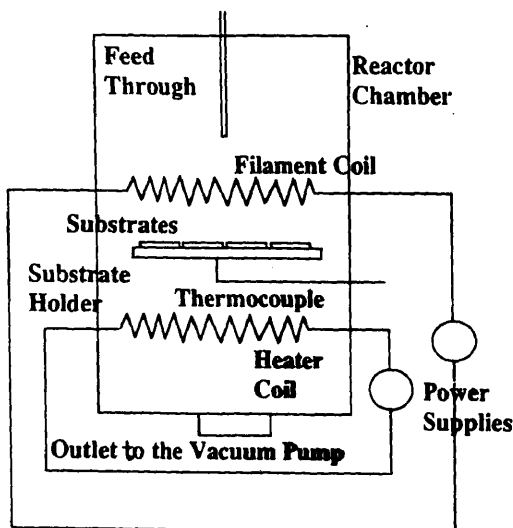


Figure 1. Schematic of the hot filament CVD system.

Table 1. Growth parameters.

Sample no.	Run no.	Pressure (torr)	CH ₄ /H ₂ ratio	Flow rate (Sccm)	Sub. temp. (°C)	Growth time (h)	Substrate type
B1	21029	50	0.5%	200	900	8	p-(111)
B2	21210	50	0.75%	200	875	8	p-(111)
B3	21222	50	1.0%	200	875	8	p-(111)
B4	30318	50	1.0%	200	875	17	p-(100)
B5	30121	50	1.5%	200	875	8	p-(111)
B6	30204	50	2.0%	200	875	8	p-(111)
B7	30513	40	0.5%	200	810	8	p-(100)
B8	30423	40	1.0%	200	875	8	p-(100)
B9	30429	40	1.0%	200	810	8	p-(100)
B10	30504	40	1.5%	200	810	8	p-(100)

2.3 Substrate preparation

The p-type <111> oriented and high-resistivity (> 100 kΩ-cm) <100> oriented silicon substrates were cleaned in acetone, etched using HF in the ultrasonic bath, and then scratched with the diamond paste (1 or 9 μm particle size) and sonicated in the ultrasonic bath. The substrates were dried and placed in the chamber.

2.4 Growth conditions

Table 1 gives the details of the growth conditions on 10 different samples selected for further analysis. As seen in this table, the methane to hydrogen ratio was varied from 0.5 to 2.0% in steps to determine the optimum ratio to yield the best structural properties. The other growth parameters such as substrate temperature, pressure during growth, growth time and flow rates were maintained constant as far as possible. Details on the fabrication and processing can be found in a thesis (Cheng 1993).

3. Raman and SEM observations

Raman spectra of CVD diamond films were obtained with an ISA JOBIN-YVON U1000 Raman spectrometer using the 514.4 nm argon line. A JEOL JSM-35 scanning electron microscope (SEM) was used to observe the surface morphology and the cross-sectional view of the CVD diamond films.

3.1 Methane concentration

Figure 2 shows a comparison of the Raman spectra based on the methane concentrations used during film deposition. Raman spectrum of B1 (0.5% CH₄) shows a sharp peak at 1330 cm⁻¹ with FWHM of 7 cm⁻¹ (a in figure 2). This spectrum also shows a very broad band centered around 1550 cm⁻¹. Spectrum c is the Raman spectrum for the sample B4 (1.0% CH₄). Again a very sharp peak at 1330 cm⁻¹ is observed

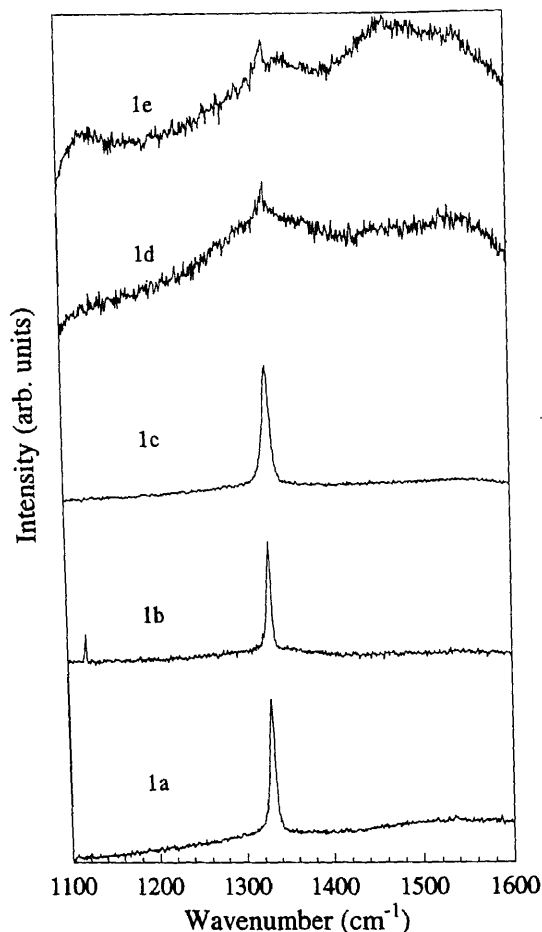


Figure 2. Raman spectra for different methane concentrations: a, 0.5%; b, 0.75%; c, 1.0%; d, 1.5%; e, 2.0%.

along with a broad band centered around 1550 cm^{-1} . A very different Raman spectrum is observed for the sample B5 (1.5% CH_4 , spectrum d). There is not only a very small diamond peak at 1330 cm^{-1} but also a well-defined broad band with a peak at 1550 cm^{-1} . Spectrum e is the Raman spectrum for the sample B6 (2.0% CH_4). This spectrum is different from that for the 1.5% CH_4 sample, indicating significant non-diamond phases of carbon. The corresponding SEM pictures for the samples B1, B2, B4 and B5 are shown in figure 3, a–d. As seen in figure 3a, sample B1 (0.5% CH_4) shows a continuous film without regular facets but large grains (average grain size $3.49\text{ }\mu\text{m}$). In a few other samples with 0.5% CH_4 , the films were discontinuous. Increasing the methane concentration to 0.75% (B2, figure 3b), we observe a dramatic change in the surface morphology. The sample contains mostly (100) facets and there is a decrease in the grain size (average grain size $1.38\text{ }\mu\text{m}$). Figure 3c shows the SEM picture of sample B4 (1.0% CH_4). It is a continuous film showing both (111) and (100) facets; however, (111) facets dominate [76% (111) facets].

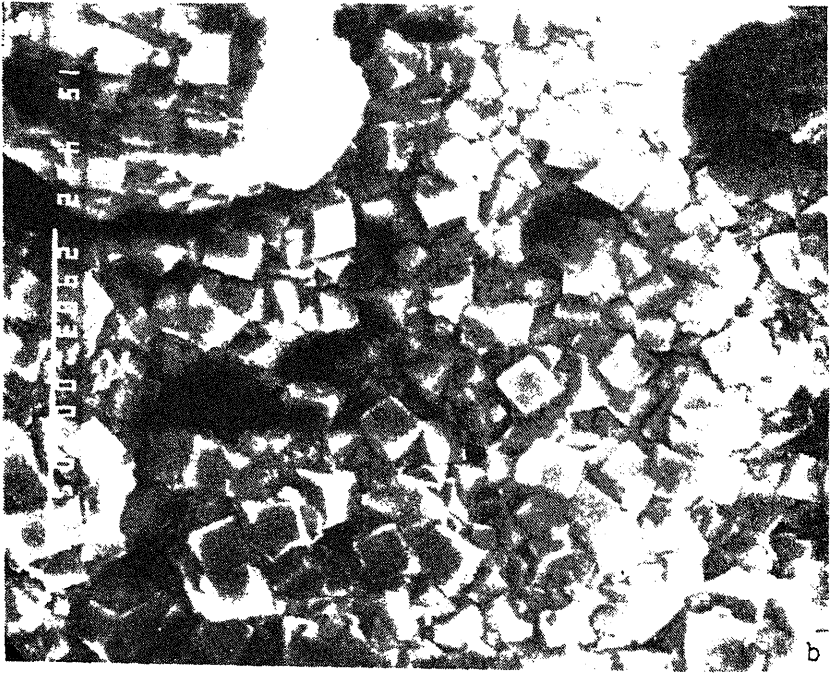
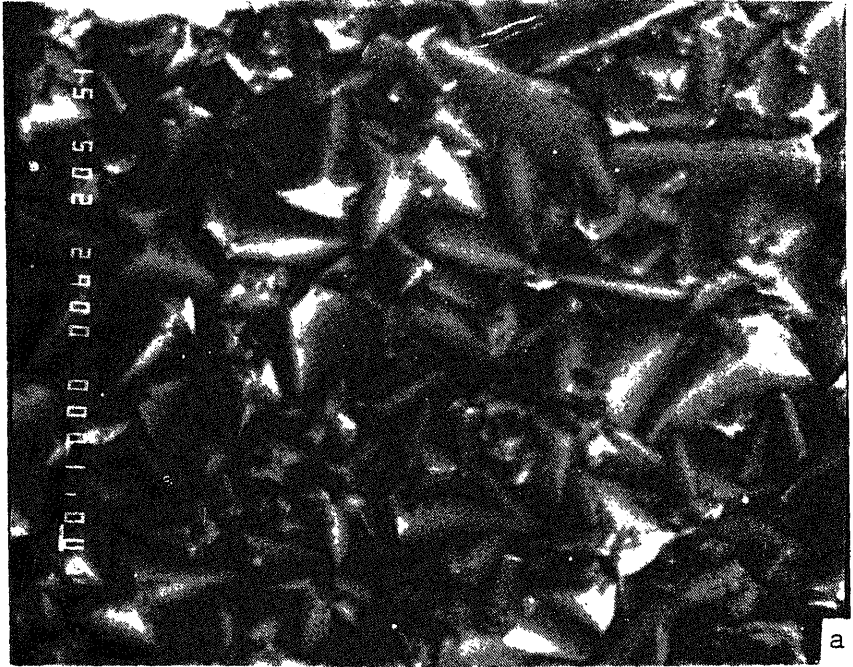
A cross-sectional view of this sample (B4) is shown in figure 4a. This figure shows that crystal sizes are large (average grain size $3.16\text{ }\mu\text{m}$) and the crystals did not coalesce to form columnar structures although the growth time was 17 h. The average thickness of this sample is only about $4\text{ }\mu\text{m}$. On the other hand, significantly different surface morphology is observed in figure 3d (B5, 1.5% CH_4). This picture shows cauliflower-like ball formation. Table 2 gives the summary of the observations of Raman spectra and SEM pictures for samples B1 to B10.

3.2 System pressure

As observed in table 1, samples B1 to B6 were fabricated maintaining a pressure of 50 torr, and the remaining four samples (B7 to B10) were fabricated maintaining a pressure of 40 torr. Two important observations are made comparing the results given in table 2: (i) high-quality CVD diamond films (judged by Raman and SEM figures) were obtained at a lower substrate temperature at 40 torr pressure, (ii) even at 1.5% methane concentration the quality of the films did not degrade at 40 torr pressure.

Table 2. Summary of the observations of Raman spectra and SEM pictures.

Sample no.	Raman spectra observations	SEM observations
B1	Diamond peaks at $1330\text{--}1332\text{ cm}^{-1}$ with FWHM of $6\text{--}11\text{ cm}^{-1}$ and a small band centered at 1550 cm^{-1}	Continuous films without regular facets but large grains ($3.49\text{ }\mu\text{m}$)
B2	Diamond peaks at $1330\text{--}1331\text{ cm}^{-1}$ with FWHM $6\text{--}9\text{ cm}^{-1}$ and almost free of non-diamond carbon phases	Non-uniform growth with small grain size ($1.38\text{ }\mu\text{m}$), (100) facets dominate
B3	Diamond peaks at $1329\text{--}1331\text{ cm}^{-1}$ with FWHM of $4.5\text{--}14\text{ cm}^{-1}$	(100) and (111) facets with grain size of $2.27\text{ }\mu\text{m}$
B4	Diamond peaks at $1329\text{--}1330\text{ cm}^{-1}$ with FWHM of $9\text{--}16\text{ cm}^{-1}$ and small band of non-diamond carbon phases	76% (111) facets
B5	Non-diamond carbon structure with small diamond peak	Cauliflower-like ball shape with voids
B6	Non-diamond carbon structure with small diamond peak	Cauliflower-like ball shape with voids
B7	Diamond peaks at 1330 cm^{-1} with FWHM of $8\text{--}9\text{ cm}^{-1}$	Mixture of (111) and (100) facets; small grain size ($1.40\text{ }\mu\text{m}$)
B8	Diamond peaks at $1329\text{--}1331\text{ cm}^{-1}$ with FWHM of $9\text{--}12\text{ cm}^{-1}$ and almost free of non-diamond carbon phases	Continuous film with large grain size ($3.40\text{ }\mu\text{m}$), (111) facets dominate
B9	Diamond peaks at $1329\text{--}1330\text{ cm}^{-1}$ with FWHM of 10 cm^{-1} and almost free of non-diamond carbon phases	(111) facets dominate (86%) grain size is about $2.55\text{ }\mu\text{m}$
B10	Diamond peaks at 1331 cm^{-1} and a band centered at 1550 cm^{-1}	Mixture of (111) and (100) facets, grain size is about $2.20\text{ }\mu\text{m}$



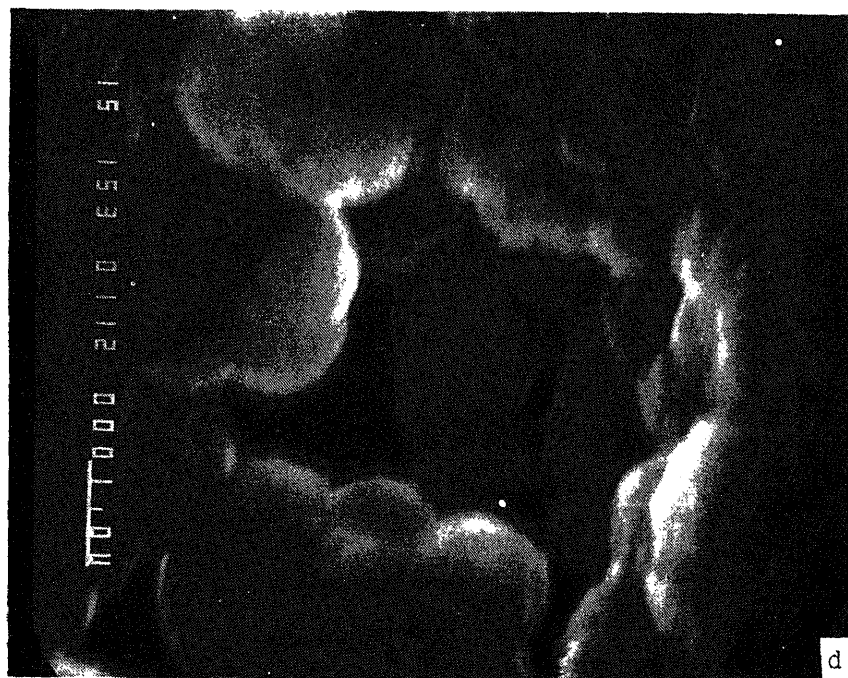
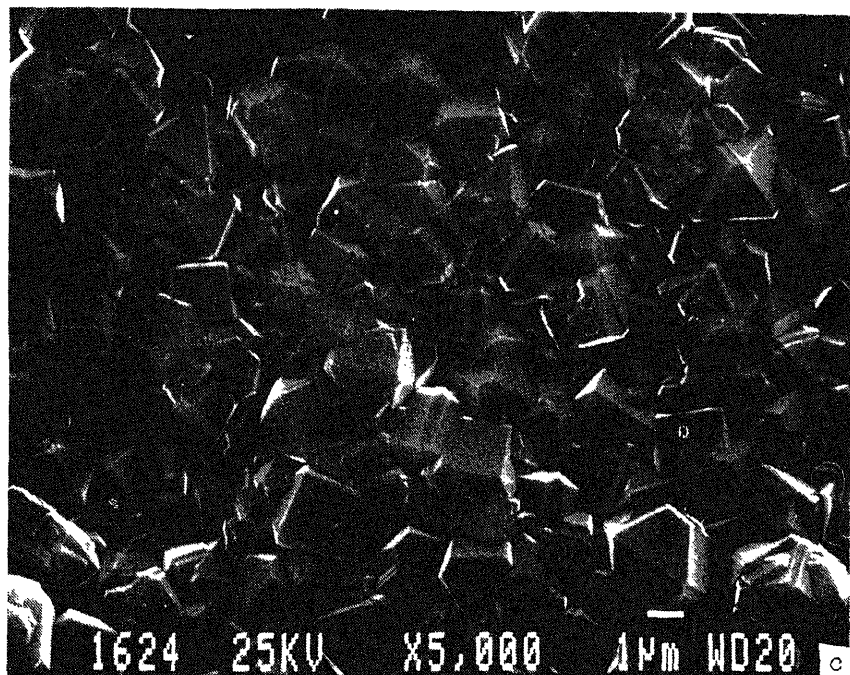


Figure 3. SEM photograph of **a.** sample B1 (0.5% CH₄), magnification 5000 ×; **b.** sample B2 (0.75% CH₄), magnification 3900 ×; **c.** sample B4 (1.0% CH₄), magnification 5000 ×; **d.** sample B5 (1.5% CH₄), magnification (× 5000).

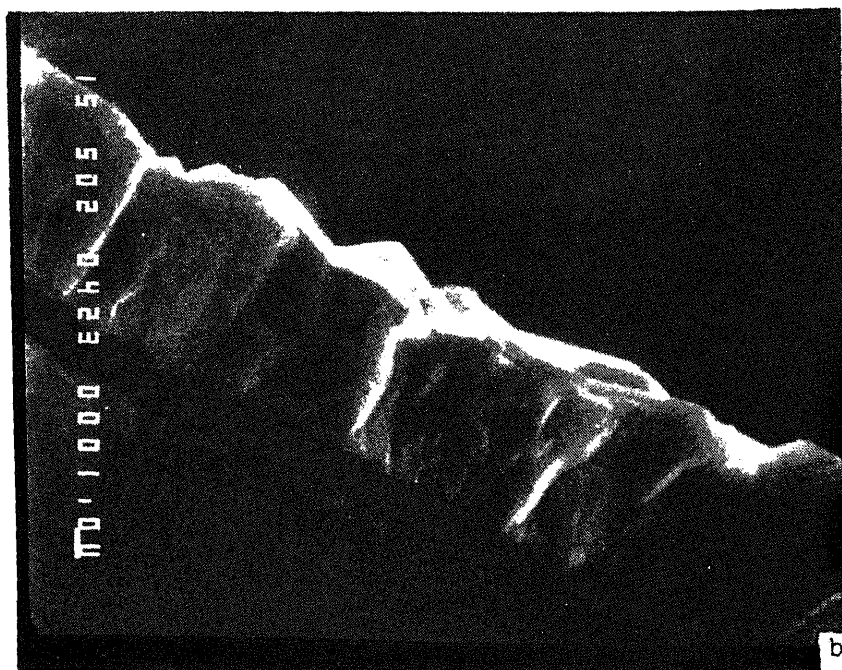
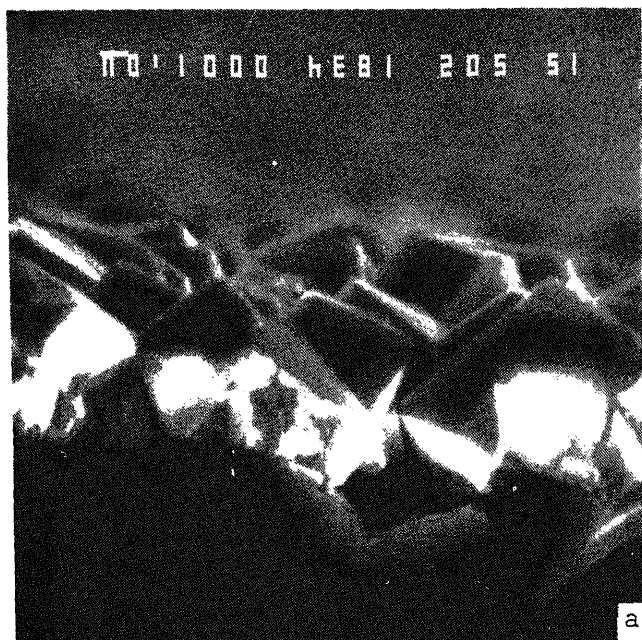


Figure 4. SEM cross-sectional view of **a.** B4 (1.0% CH₄), magnification 5000 ×; **b.** B8 (1.0% CH₄), magnification 5000 ×.

Substrate temperature

Comparing samples B8 and B9 (875°C vs 810°C) it is observed that the average grain size of the diamond crystals increases from $2.55\mu\text{m}$ with increase in substrate temperature. The quality of the films grown at 810°C substrate temperature appears to be superior (see figure 4b, a cross-sectional SEM picture of sample B8), showing columnar growth and compact structure.

Sheet resistivity

Electrical characterization of polycrystalline CVD diamond films is necessary to determine the feasibility of these films for high-temperature electronic applications.

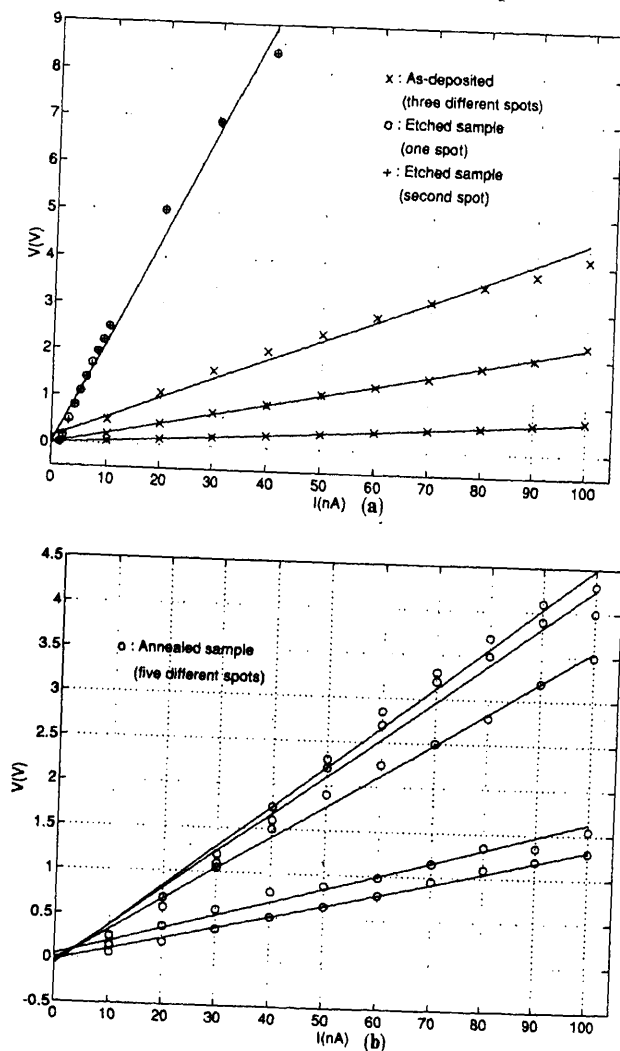


Figure 5. Current-voltage characteristics of a. a typical as-deposited sample measured by four-point probe techniques; also shown is the characteristic after etching chemically; b. sample after annealing in vacuum at 850°C for 30 min.

A common method for measuring the sheet resistance of thin films is the four-point probe method. Details of the measurement procedure are described elsewhere (Shrotriya 1993). Figure 5a shows the current-voltage characteristics of a typical as-deposited diamond thin-film sample measured by four-point probe techniques. The growth parameters for this sample were as follows: methane to hydrogen ratio 1%, system pressure 40 torr, substrate temperature 850°C, filament temperature $\geq 1850^\circ\text{C}$, high-resistivity ($> 100\text{ k}\Omega\text{-cm}$) $< 100 >$ oriented silicon substrates.

The three different curves for the as-deposited sample represent measurements on three different spots on the same sample. Assuming a thickness of $10\text{ }\mu\text{m}$ for this sample the average resistivity for the as-deposited sample is $8.68 \pm 6.56 \times 10^4\text{ }\Omega\text{-cm}$. Such a large variation in the resistivity is due to either graphitic regions in between diamond crystals or hydrogen absorbed on the surface. Also shown in this figure is the current-voltage characteristic of a chemically etched sample. The sample was etched in a saturated solution of CrO_3 and H_2SO_4 for 1 h. As seen in this curve, the data from two different spots overlap. The sheet resistivity increased to $7.90 \times 10^5\text{ }\Omega\text{-cm}$. Such dramatic changes in the sheet resistivity as well as surface texture and composition of the film after chemical etching are described in detail in another paper (Kulkarni *et al* 1994). Figure 5b shows the current-voltage characteristics of the same sample after it was annealed in vacuum at 850°C for 30 min. Again the five curves correspond to five different spots on the same sample. The average sheet resistivity of this sample increased to $1.10 \pm 0.57 \times 10^5\text{ }\Omega\text{-cm}$ after annealing. In general, we have observed sheet resistivities in the range of 10^2 to $10^5\text{ }\Omega\text{-cm}$ for as-deposited undoped diamond films.

5. Discussion

5.1 Nucleation

The nucleation and growth of CVD diamond films on silicon substrates is strongly dependent on substrate preparation (Williams and Glass 1989). We used diamond pastes with different particle sizes ($9\text{ }\mu\text{m}$ and $1\text{ }\mu\text{m}$) to scratch the silicon substrates. The samples B1 to B5 were scratched with $9\text{ }\mu\text{m}$ diamond paste and had rougher surfaces. From figure 4a (cross-sectional SEM picture), one can estimate a nucleation density of about $1.3 \times 10^7\text{ cm}^{-2}$ (8 crystals within $22\text{ }\mu\text{m}$ length). The nucleation density is estimated to go up by seven orders of magnitude (10^4 to 10^{11} cm^{-2}) from unscratched silicon substrates to heavily scratched silicon substrates (Kweon *et al* 1991). It is known that CVD diamond growth on silicon causes the development of a $\beta\text{-SiC}$ (cubic zinc-blended crystal structure) interlayer between silicon and diamond in the initial stages of growth (Belton *et al* 1989; Meilunas *et al* 1989). A clear understanding of the nucleation of diamond on silicon substrates is crucial for the development of high-quality epitaxial diamond thin films on silicon substrates.

5.2 Growth

Depending on substrate preparation, growth method and growth conditions large-grained ($> 1\text{ }\mu\text{m}$) polycrystalline to submicrocrystalline ($< 0.1\text{ }\mu\text{m}$) CVD diamond thin films are grown. Epitaxial growth of single-crystalline diamond on non-diamond

substrates such as silicon has remained a challenge that has to be addressed if high-temperature diamond electronic devices are to be fabricated and used in everyday life. The dependence of the structural properties of the film on three important growth parameters, viz. methane to hydrogen ratio, substrate temperature and system pressure, are described in detail, comparing our experimental results with the results of other investigators.

2a Methane concentration: With increasing methane concentration from 0.5 to 0.9% dramatic changes are observed in both Raman spectra (figure 2) and surface morphology (figure 3). A few other investigators have also observed the broadening of the diamond peak (larger FWHM) and increasing intensities of peaks due to non-diamond carbon phases with an increase in the methane concentration in HFCVD diamond films (Mercier *et al* 1991; Kweon *et al* 1991). With increasing methane concentration (up to 1.0% or 1.5%) the growth rate increases to yield continuous films with regular facets. However, very high methane concentrations (> 1.5%) increase the formation of graphitic phase as a direct consequence of a decrease in atomic hydrogen flux. Both Raman and SEM data substantiate this observation. On the contrary, for methane concentrations below 0.5%, the etching rate of diamond and graphite due to atomic hydrogen exceeds the growth rate resulting in discontinuous films. The decrease of grain size with increasing methane concentration (from 0.5 to 0.75%) is attributed to carbon supersaturation in the gas phase and nucleation enhancement. Zhu *et al* (1990) observed the surface morphology of CVD diamond films to indicate that triangular (111) faces changed to square (100) faces when methane concentration was increased from 0.5 to 2.0%. These authors observed ball-shape formation at higher substrate temperatures and higher (5%) methane concentration. Our results agree with those of Zhu *et al* (1990) at high methane concentrations, but there is a disagreement about the types of facets, (100) vs (111), at lower methane concentrations. Similar to our results, Spitsyn *et al* (1981) observed (111) facets for high methane concentrations and low substrate temperatures and (100) facets for low methane concentrations and high substrate temperatures. The formation of facets is a function of carbon supersaturation, nucleation rate, carbon atom mobility on the surface, and surface restructuring processes such as fusion and absorption among secondary crystallites (Kobashi *et al* 1988).

2b Substrate temperature: Substrate temperature controls the mobility of the carbon atoms on the growing surface and hence affects nucleation, surface restructuring and quality thin-film growth. It is well known that there is a working temperature range (800–1000°C) for growing large-grain-size (1–5 µm) diamond thin films by CVD methods (Kondoh *et al* 1992). Very high substrate temperatures (> 1300°C) result in the formation of graphitic carbon (Spitsyn *et al* 1981) and grain sizes of diamond thin films decrease with decreasing substrate temperatures (200 nm at 650°C, 10–20 nm at 500°C). We observed an increase in average grain size from 0.55 µm to 3.40 µm with increasing substrate temperature from 810°C to 875°C under identical growth conditions.

2c System pressure: The system pressure during growth affects mainly the flux of atomic hydrogen to the growing surface and the recombination of atomic hydrogen

to form molecular hydrogen (Mercier *et al* 1991). At high pressures (> 50 torr) the hydrogen flux decreases resulting in graphite formation and at low pressures (< 50 torr) the hydrogen flux increases to result in efficient etching of graphite form of carbon. However, increasing hydrogen flux also enhances hydrogen incorporation in diamond films. Large-grain-size ($10\text{ }\mu\text{m}$) diamond crystals are typically grown at pressures from 20 to 100 torr depending upon other growth parameters and the system used. Our limited experimental results at two different pressures (50 torr and 40 torr) showed a remarkable improvement in the quality of the films at 40 torr compared to those films grown at 50 torr.

Some other growth parameters such as filament temperature, gas flow rates, biasing of the substrate, filament to substrate distance and types of gases used also affect the quality of the diamond thin films to a limited extent.

5.2d Sheet resistivity: The sheet resistivities of the as-deposited undoped diamond films are reported to be in the range of 10^2 – $10^6\text{ }\Omega\text{-cm}$ (Landstrass and Ravi 1989a; Ramesham *et al* 1991). The low sheet resistivity of undoped CVD diamond films is attributed either to the hydrogen passivation of defect states (Landstrass and Ravi 1989b; Albin and Watkins 1990) or to the presence of disordered graphitic regions between the grains (Shiomi *et al* 1990; Muto *et al* 1991; Kulkarni *et al* 1994). This low resistivity of as-deposited films can be enhanced significantly either by annealing beyond 800°C to remove hydrogen from the surface layers (Landstrass and Ravi 1989a; Albin and Watkins 1990) or by chemically etching the films in a saturated solution of CrO_3 and H_2SO_4 (Muto *et al* 1991; Kulkarni *et al* 1994). The sheet resistivities in the range of 10^2 – $10^5\text{ }\Omega\text{-cm}$ observed for the undoped diamond films in our experimental work agree well with the reported values. An order-of-magnitude increase in the resistivity was observed in the chemically etched sample. In several chemically etched samples the very high resistivity could not be measured because of the limited scope of the measurement techniques.

6. Conclusions

Chemical vapour deposition of diamond thin films for a variety of applications has advanced rapidly in the last decade. However, large-scale commercialization of this vapour-phase-growth technology is yet to be realized. The major hindrance to the development of this technology has been the inability to grow high-quality single-crystalline diamond films on economically inexpensive non-diamond substrates. This review paper has attempted to summarize recent results in chemical vapour deposition of diamond thin films on silicon substrates. In particular, the dependence of the characteristics of the films as determined by Raman spectroscopy and scanning electron microscopy on growth parameters such as methane to hydrogen ratio, substrate temperature and system pressure has been discussed in detail. Dramatic changes were seen in the Raman spectra (crystalline diamond to graphitic and amorphous carbon) as well as surface morphology (faceted structures to cauliflower-type ball shapes) with changes in methane to hydrogen ratio of 0.5% to 2.0%. The sheet resistivities of the films were in the range 10^2 – $10^4\text{ }\Omega\text{-cm}$ for the as-deposited samples. The effect of chemical etching and annealing on the sheet resistivity have been discussed. The correlation of the electrical properties of these films with the structural properties which in turn depend on the growth parameters will lead to

better understanding of the control of the electrical characteristics of these films for semiconductor device applications.

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The magnetic metrology of materials—A review

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Abstract. This paper gives a survey of the present state and new aspects of the measurement techniques for the characteristics of magnetic materials (except for recording materials) with several examples. Particular attention is paid to the aspects of reproducibility and traceability to SI units, and to the current trend of quality assurance and standardization.

Keywords. Magnetic materials; measurement techniques.

Introduction

A great variety of methods for the determination of the magnetic properties of materials is in use. The characteristics of the methods vary with the purpose (research, calibration, acceptance tests or quality control measurements), the sample's properties (shape, size, permeability, etc.), and the quantities to be measured (coercivity, remanence, saturation magnetization, permeability, anisotropy, magnetic losses, maximum energy product, magnetoelastic properties, etc.).

Table 1 lists the main materials (except recording materials which we shall not treat in this paper) in use together with the quantities of interest. Most of the measurement methods for their determination are well known, and experience has been gained in using them. However, modern electronics has given an impetus to the development of rationalized as well as more complicated measurement techniques. Today's powerful computers and finite element method (FEM) programs make a more detailed estimate of the error characteristics of the magnetic circuits used for the measurements possible, thus bringing about modifications of traditional methods.

The following survey reports, with the help of examples because completeness is impossible within the frame of this paper, on fundamental aspects for the measurements in DC and AC fields, tracing to the SI units, and standardization. We will focus on the methods for characterization of the properties relevant for applications rather than basic physical characteristics such as domain structure, Mössbauer spectrum, etc.

Basic aspects, tracing to SI units

In principle there are three metrological concepts one of which is given priority depending again on the purpose (see table 2). In magnetic materials metrology, the repeatability concept reigns in materials development and research labs, reproducibility where trade is involved, and, most rarely, accuracy where absolute values or natural constants are aimed at.

The main quantities for the determination of magnetic material properties are two: the magnetized state, i.e. the magnetic polarization J , and the driving force necessary

Table 1. Main categories of magnetic materials and the most important quantities to be measured.

Soft	Hard magnetic materials	Feebly
Electrical steel	AlNiCo	Para- and diamagn.
NiFe	Ferrites	materials Stainless steel
Soft ferrites	RECo	Brass, Copper
Amorphous	NdFeB	
Saturation polarization J_s		Susceptibility
DC hysteresis loss	Remanence	
AC power loss and apparent power	Coercivity (BH) _{max}	
Rotational power loss	Stability	
$B(H)$ curve		
Magnetostriction		

Table 2. Metrological concepts and their priorities.

Concept	Priority with
Repeatability	Materials research and optimization
Reproducibility	Methods laid down in standards, quality control, acceptance tests, intercomparisons
Accuracy	Realization of units, absolute characteristics of materials, natural constants

to reach that state, i.e. the magnetic field strength. Table 3 lists the main methods for the measurement of these two quantities. However, only a few of the H methods are applied to materials, viz. Hall probes, and, most of all, inductive methods. Besides these, the indirect method of determining H from the magnetizing current is very common in the cases where the demagnetizing field is small (closed magnetic circuit) or is well known (ellipsoidal specimen). The inductive method requires integration of the signal. The magnetic field strength H inside the specimen can be measured approximately only close to its surface. These points will be considered in the next section.

Recently, tracing the magnetic units to the SI system of units is considered more and more important. The ISO 9000 standards system is increasingly applied for quality assurance not only in industrial quality control but also in research labs. The laboratories authorized for the realization, maintenance and dissemination of the national units and their tracing to the international level are national laboratories such as the NPL in New Delhi or the PTB in Braunschweig, Germany. In our field of magnetic materials metrology, the tracing to SI units is in no way a problem of the electrical and mechanical units forming the basis for our derived magnetic units because those are known to a much higher accuracy than that to which material properties are, in view of their scatter, definable. The magnetic circuit is mostly the main problem.

Table 3. Survey of the most important methods for the measurement of magnetic field strength H and magnetic polarization J . (for details and references see Ahlers and Sievert (1991), Weyand (1991) and Zijlstra (1967)) and for the study of the magnetic structure of the material. (Less known abbreviations: SST, single sheet tester; VSM(VCM), vibrating sample (coil) magnetometer).

<i>Magnetic field strength H:</i>	<i>Magnetic polarization J: (Material characteristics)</i>
<i>Induced voltage</i>	<i>Force</i>
Rotating coil, search coil	Gouy and Faraday balance; torque, torsion, vibrating reed magnetometer
<i>Indirect measurement</i>	<i>Induced voltage</i>
From magnetizing current (defined magn. circuit)	Ring core, Epstein, SST, permeameter, VSM, SQUID, VCM
<i>Galvanomagnetic sensors</i>	<i>Others</i>
Hall effect, magnetoresistance, magnetotransistors, etc.	Astatic magnetometers Hall probe, fluxgate or torsion sensor, Faraday rotation, Kerr effect, ESR, Mössbauer
<i>Ferromagnetic sensors</i>	
Fluxgate, thin-film, magnetostrictive- optoelectronic sensors (optical fibres)	
<i>Quantum effect sensors</i>	<i>For structural studies:</i>
NMR, ESR, Zeeman effect, Faraday rotation, RF- and DC-SQUID	Kerr and Faraday optcl. eff., bitter technique, scanning electron microscopy, neutron scattering

For the calibration of field strength measuring devices, almost only the nuclear magnetic resonance (NMR) technique is applied, making use of the results of precision fundamental experiments for the determination of the gyromagnetic coefficient of the proton (Weyand 1991). This follows the general trend of basing all units on fundamental constants and quantum effects. Commercial NMR instruments are available, allowing, when due caution is exercised for field homogeneity and equivalence, an accurate calibration of secondary standards such as H sensing coils or Hall probes.

The calibration of polarization measuring devices depends on their principle. Force sensing devices can be calibrated with the help of a reference mass. The most-in-use inductive method requires, besides the calibration of the search coil, calibration of the flux integrator. Formerly the ballistic galvanometer was in common use as the flux integrator whereas nowadays electronic integrators are preferred. Fluxmeters are calibrated either by means of a mutual inductor which is calibrated itself electrically, or otherwise by means of a capacitor discharge. Modern electronics have opened a more convenient and precise solution to this problem. The electronic calibrator developed by Rahf (1989) which in turn is calibrated by precision tracing to time and voltage standards, generates trapezoidal voltage $\times$ time curves with controllable slope and duration, and allows the calibration of fluxmeters to better than 2×10^{-4} .

In order to avoid the effort of tracing back the indication of a magnetometer directly to SI units, reference samples, in particular nickel samples, are applied (Sievert *et al* 1990a). The saturation polarization of Ni is known accurately from earlier extensive investigations (Bennet *et al* 1978; Graham 1982) and amounts to $0.615 \text{ T} \pm 0.0005 \text{ T}$ at 23°C . We studied the error sources for the case of cylindrical Ni reference samples used in the air gap of an iron core magnet. The calibration of such cylindrical reference samples which are available from the Bureau of Reference of the EU (Commission of the European Union, Dir. Gen. Science, Research and Development, Bureau BCR, Rue de la Loi 200, B 1049 Brussels, Belgium) can be carried out with a relative uncertainty of 0.15% (σ_1), and the subsequent calibration procedure in laboratories using these samples should be possible with a relative uncertainty of 0.5% (Sievert *et al* 1990a).

3. Excitation, sensors and measurement of the electric signal

Measuring magnetic materials involves four partial problems (see also figure 1 with the exemplary ring specimen):

- excitation of the specimen with specific conditions determined by the specimen's properties and geometry and for DC or AC fields;
- type of sensors, their geometry and position;
- the electrical measurement including integration;
- the evaluation.

The first two points refer to the magnetic circuit. We distinguish between open (samples in solenoids, superconducting or Bitter magnets, spherical sample in an electromagnet) and closed (ring cores, Epstein frame, sheet samples in yokes, cylinders clamped between the poles of an electromagnet, etc. (for ref. see e.g. table 4, 404–4,

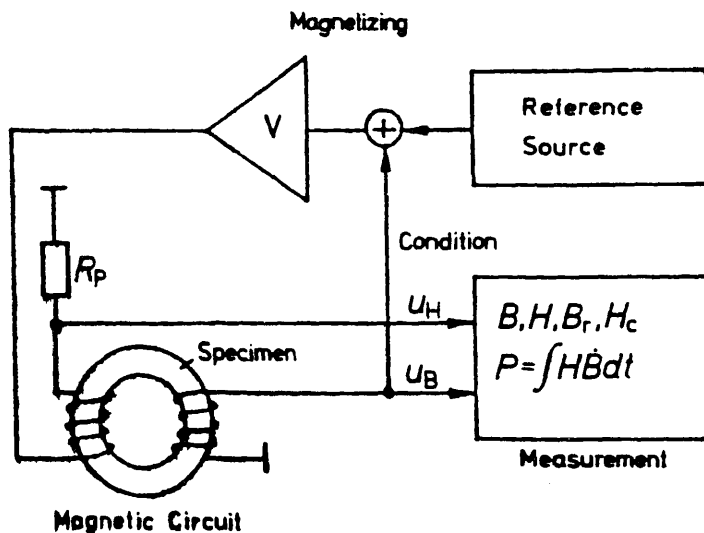


Figure 1. Basic elements of a magnetic circuit for measuring magnetic materials.

Table 4. IEC standards on methods of measurement for the magnetic properties of materials (abbreviated titles).

404-2	: Magnetic, electrical and physical properties of magnetic sheet and strip (1978, currently under revision)
404-3	: Magnetic properties of magnetic sheet and strip by means of a single sheet tester (1992)
404-4	: D.C. magnetic properties of solid steels (1994)
404-5	: Magnetic properties of magnetically hard (permanent magnet) material (1993)
404-6	: Magnetic properties of isotropic nickel-iron soft magnetic alloys, types E1, E3 and E4 (1986)
404-7	: Coercivity of magnetic materials in an open magnetic circuit (1982)
404-10	: Magnetic properties of magnetic sheet and strip at medium frequencies (1988)

2, -3, and -5, respectively)) magnetic circuits. The methods of exciting and sensing depend decisively on whether we have an open or closed magnetic circuit.

DC measurements on small ferromagnetic and on feebly magnetic samples are preferably carried out in an open magnetic circuit applying force (Gouy or Faraday balance) or inductive methods for sensing of the polarization. In iron-free circuits, the field strength is conveniently determined from the magnetizing current and the coil constant of the magnetizing coil, whereas in iron core magnets usually a separate sensor for the field has to be used.

The closed magnetic circuit is the one preferably used where quality control is aimed at and averaging over a greater amount of material is requested. Thus most of the magnetic standards treat the closed circuit (see table 4). The following considerations essentially hold for the DC and AC case equally.

The closed magnetic circuit may consist completely of the specimen (ring cores or Epstein specimens). In this case H can easily be determined from a measurement of the magnetizing current on the basis of the simplified Ampere's law: $H = N_1 \cdot I_1 / l_{\text{eff}}$, with N_1 number of turns of the magnetizing winding and I_1 magnetizing current. The effective magnetic path length l_{eff} is, in particular in the less homogeneous Epstein sample, an approximation for the path along which the magnetic potential $N_1 \cdot I_1$ drops. In so far this simplification always implies a systematic error. Epstein results are, for instance, too high by about 4% for low inductions and, for a high induction, too low by 4% to 10%, depending on the permeability of the sample (Sievert 1984). In other setups the specimen may make up only a part of the magnetic circuit (single strip (or sheet) testers, permeameters, see table 4, 404-3 and -4, for reference), excited between flux closure yokes.

In this case also the field strength can be determined from the magnetizing current, the magnetic potential dropping along the path through the yokes can be neglected (Sievert *et al* 1990b). However, where relatively high fields are to be reached as in permeameters and electromagnets, tangential H sensing coils or also Hall probes are applied for the measurement of H at the sample's surface. This method involves, in principle, a systematic error which can be considerable, if the magnetizing winding is wound on the yokes. However, if the winding surrounds the specimen uniformly,

air gaps are kept small, and highly permeable yokes provide a small field gradient transverse to the specimen's surface, this error may be small. It increases with the permeability of the sample, and thus depends on the flux density inside the sample. In special cases such as two-dimensional excitation and measurement on steel sheet samples where the conditions mentioned before cannot be met, double H coils for extrapolation to the surface may be necessary, or Rogowski-Chattock potential sensing coils (Zijlstra 1967) can be used to come closer to the surface. Calculating the field distribution by means of FEM for the area where the sensors are to be located is often a very valuable help for the assessment of the accuracy of the sensing.

As to the homogeneous and defined magnetizing of the sample, certain conditions must be met. In the DC case which, in fact, is usually a quasi-DC exciting, the change of the field strength must be controlled to be sufficiently slow in order to avoid eddy currents. This can be obtained with the help of a feedback which provides constant steps of the flux density change (Ahlers and Hartwig 1985). For permanent magnet material with very high coercivity such as NdFeB, separate pulse magnetizers or superconducting magnets must be used for the initial magnetizing up to saturation. Thereafter the sample is to be moved into the sensing coil system whereas the measuring device (flux integration) must already be working simultaneously. In the AC case, the magnetic loss in the sample depends on the distribution of higher harmonics on the H and J signals which in turn depend on the ratio of the output impedance of the power supply to the input impedance of the magnetizing circuit. It is therefore conventionally agreed that the flux density is to be changed sinusoidally (which means using a voltage source), which can be made, for instance, by an electronic negative feedback. It corresponds to a form factor value of the J signal of 1.1107. This condition can hardly be met for high flux densities where the power supply reaches its current limit. Deviations from symmetry of the flux density involve even harmonics and lead also to considerable errors (Ahlers and Sievert 1984).

Modern electronics are a decisive help in meeting the conditions required for magnetizing the sample. However, still more they are essential for due signal treatment and evaluation. After, in a first step, analog electronics had entered magnetic metrology, there is nowadays no alternative to digital procedures which were first introduced by Capptuller *et al*, if one wishes to measure efficiently, fast and precisely (Capptuller 1971; Capptuller and Ahlers 1975). By this we understand, in the DC case, voltage-to-frequency conversion and then counting of the signal which includes the integration process, and in the AC case, analog-to-digital conversion of the signal from the sensors and digital evaluation in a computer. The main advantages are the following: easy to calibrate using a precise DC voltage source, absolutely linear and time-independent integration and multiplication of the power measurement. However, for power measurements one still has to check that the preamplifiers do not change the phase angle which may, where the power factor is low, cause considerable errors.

4. Standardization

Methods to be standardized should be as simple and reproducible as possible. Sometimes research activities and intercomparisons precede the publication of a standard (Sievert 1984; Sievert *et al* 1990b). Table 4 presents a survey of existing IEC standards in the field of magnetic materials metrology. Naturally in this list methods

used for quality tests of economically important materials are predominant. Thus magnetic steel sheet plays the main role. Fourteen of the 40 national members of EC take part in preparation and repeated revision of these standards. Other important standard systems comprising magnetic standards are the ASTM (US), BS (UK), DIN (Germany), EN (European Union), GOST (former USSR) and JIS (Japan).

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Selective semiconductor sensors for reducing and oxidizing gases

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Abstract. The ever-increasing need for sensors capable of detecting and monitoring toxic and flammable gases is presented and the various techniques available are introduced. Semiconductor devices based on tin dioxide, which potentially have many desirable characteristics, are discussed in detail with particular reference to the work in Swansea which has focused on the problem of selectivity.

Keywords. Gas detection; tin dioxide; selective sensors.

1. Introduction

There can be no doubt that the need for sensors to monitor a wide variety of measurands will continue to grow. This is illustrated in figure 1 which shows the predicted growth in the European sensor market for the decade from 1990. The world market will undergo similar growth and is expected to be worth in excess of £24 billion by the year 2000 (Harmer Associates). The market in the specific area of gas sensors is expected to undergo a similar percentage increase, the need occurring in an extremely wide variety of areas including the mining, petrochemical and gas industries; emission monitors; automotive sensors; and medical and domestic applications. This is due in part to increased public awareness, but is mainly a result of associated legislation. These requirements have, in turn, led to a vast amount of world-wide interest in gas sensor research and development. Gas sensor research is one of the truly interdisciplinary fields in modern science calling upon the expertise of, amongst others, chemists, physicists, and electrical and mechanical engineers. There are currently several technologies available for the detection of gaseous species and these are listed in table 1 together with a brief summary of their mode of operation. All of these sensor types possess at least some of the characteristics that are desirable in a commercially viable device, including high sensitivity, fast response, low power consumption, low ambient temperature and humidity dependence, negligible drift, longevity, low cost and selectivity. It should be noted however that few, if any, sensors possess all of these characteristics and that the precise requirements for any sensor will depend on the specific application. For example, if a sensor is required to monitor a toxic gas such as carbon monoxide (CO) then it is usually the threshold limit value (TLV, the time-weighted average concentration to which exposure is considered safe for a specified period (in this case 8 h, i.e. a normal working day)) that is of interest, which in this case is 50 ppm. For other gases this can be much lower, for example nickel carbonyl ($\text{Ni}(\text{CO})_4$) where the TLV is 0.001 ppm. In these cases it is necessary to have a highly sensitive sensor capable of monitoring such low levels. Conversely, if flammable gases are to be detected then it is usually the lower explosive limit (LEL, the concentration in air above which an explosion is possible given a

European sensor market by parameter

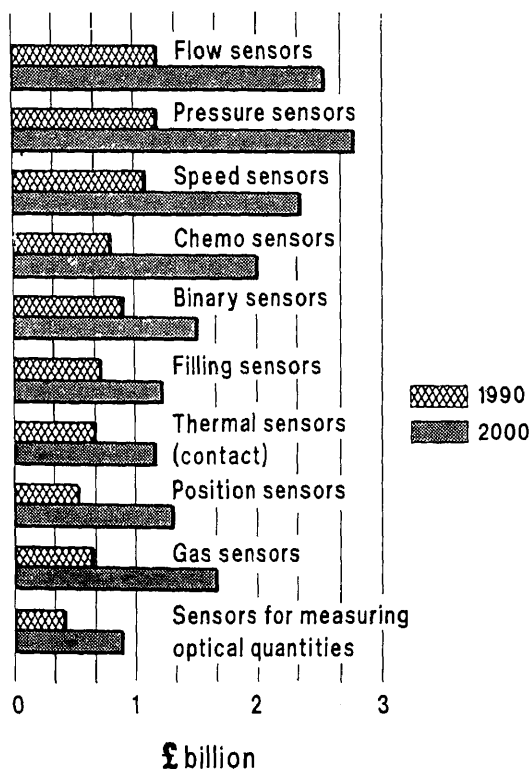


Figure 1. The expected growth in the European sensor market by parameter for the decade from 1990.

source of ignition) which is of interest and for methane (CH_4) this is 4% or 40,000 ppm. It is feasible that sensors could be used in these situations where the sensitivity is at least three orders of magnitude less than in the previous cases. Another example is that of power consumption. For an installed instrument or system where mains power is readily available then power consumption is generally a minor consideration. However, the requirement for low-power devices becomes critical if portable, battery operation is envisaged.

The last category of sensors described in the table are the semiconductor devices, which are usually based on tin dioxide (SnO_2). These devices are amongst the world's best selling type of gas sensor and they have the potential to exhibit many of the previously cited characteristics. However, one of their major disadvantages has been a lack of selectivity which has led to their being ignored by large numbers of sensor users. It is this specific problem that has been studied in Swansea.

2. Tin dioxide as a gas sensing element

Tin dioxide occurs naturally as cassiterite which has a rutile-type structure. Its main industrial uses are in the ceramics industry where it is used as an opacifier and

Table 1. Common types of gas sensor and their mode of operation.

Gas sorption	where a gaseous species is irreversibly adsorbed onto a compound, often by way of a chemical reaction producing a change in one of the physical properties of the material, such as colour
Photophysical	for example, infrared or ultraviolet spectrophotometry in which a specific molecular transition is monitored; this (in addition to the first method) is becoming increasingly linked with fibre-optic technology
Catalytic	in which gases react on a catalytic filament via an exothermic process, the resulting temperature increase being monitored via a corresponding resistance change in the filament
Electrochemical cells	where gases react at electrodes to produce electric currents
Ion-selective electrodes	across which a potential is established when the gas is exposed to wet electrodes
Micro balances	here, gases are adsorbed onto a coated piezoelectric crystal, the resulting weight change causing a frequency shift from the fundamental
Field-effect transistors	can be closely related to several of the other methods mentioned here but made possible by silicon technology and typified by such devices as ion-selective field-effect transistors (ISFETs), chemical FETs (CHEM-FETs) and enzyme FETs (ENFETs)
Semiconductors	in which a reversible reaction of the gas at the semiconductor surface results in a change of one of its electronic properties, usually conductance

pigment base, and in the electronics industry where it is used as the transparent electrodes in various applications such as liquid crystal displays. It is a wide-band-gap semiconductor ($\Delta E \sim 3.5 \text{ eV}$) in which oxygen vacancies confer n-type properties. When exposed to air at ambient or elevated temperatures oxygen is adsorbed from the air in one or more of the following forms: O^- , O^{2-} , O_2^- or O_2^{2-} . These oxygen species are available to react with reducing gases, the associated electrons being returned to the conduction band resulting in a resistance decrease. It is this change in resistance that is monitored electrically to give a warning light, alarm or readout. Following reaction, oxygen is again adsorbed from the air and the process continues. This can be visualized as a cyclic reaction, and is shown diagrammatically in figure 2 for the case of carbon monoxide (CO), where it is oxidized to produce carbon dioxide (CO_2). The problem is that many other reducing gases can also be oxidized at the surface resulting in similar resistance changes. Several mathematical models have also been proposed which describe the operation of these devices (Clifford and Tuma

1982; Morrison 1987). Oxidizing gases can also affect the resistance of this material by competing with the oxygen adsorption process. In these cases resistance increases are usually observed.

Early work in this area concentrated on achieving a degree of selectivity by temperature control. This is shown in figure 3 for a pure tin dioxide sample (Firth *et al* 1975). At low temperatures tin dioxide is too resistive to be useful as a sensor element and the reactions are too slow to be of practical use. At high temperatures the response to any gas becomes undetectable due to the low resistivity arising from thermal promotion of electrons to the conduction band. As temperature is increased from ambient a response to CO is observed above $\sim 200^{\circ}\text{C}$ and this increases, reaching a peak at $\sim 400^{\circ}\text{C}$. No response to methane is observed below temperatures of 300°C and the response to this gas peaks at $\sim 500^{\circ}\text{C}$. From figure 3 it can therefore be seen that operating a sensor composed of tin dioxide at a temperature of $\sim 300^{\circ}\text{C}$ gives a sensor which will selectively detect CO in preference to CH_4 . It should be noted however that at no temperature is the opposite selectivity observed for this sample.

From this description it can be seen that it is necessary to operate devices of this type at elevated temperatures typically in the range $200\text{--}400^{\circ}\text{C}$. This requires the use of a substrate which provides mechanical support for the active material and incorporates both a heater and means of interrogating the material. A typical commercially available substrate is shown in figure 4. Deposited on one face of the

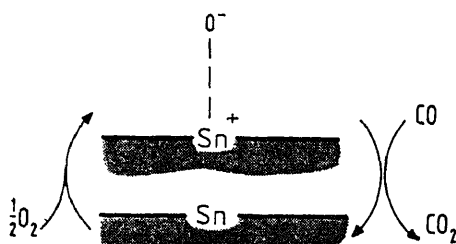


Figure 2. A diagrammatic representation of the reaction occurring on a tin dioxide surface for the case of carbon monoxide.

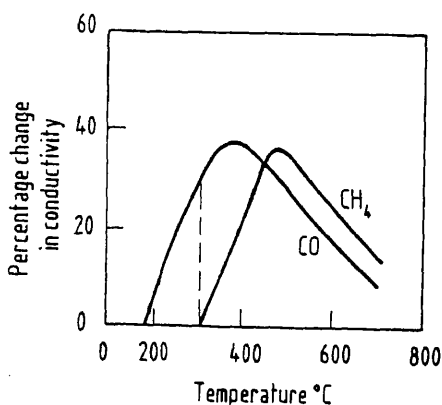


Figure 3. The percentage change in conductivity versus temperature for a pure tin dioxide gas sensor in 100 ppm inclusions of carbon monoxide and methane.

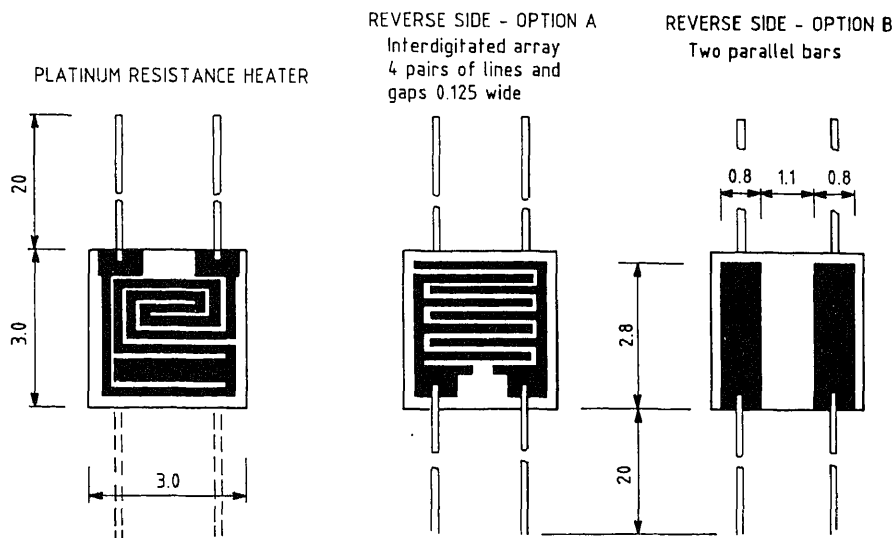


Figure 4. A commercially available sensor substrate (produced by Rosemount Engineering, Bognor Regis, UK) showing the heater track and contact array options.

A 3 mm × 3 mm × 0.6 mm alumina chip is a platinum resistance heater and on the other side a choice of either two parallel platinum pads or an interdigitated array. The latter option is used if active materials with higher resistances are to be measured. These substrates are easily capable of reaching desired operating temperatures and to achieve a temperature of ~300°C require about 1 watt. One of the major problems associated with the substrate is price. The active sensor material itself costs fractions of a penny whereas the above substrates retail at ~£40. Several groups around the world, including our own, are therefore looking at methods of producing cheaper in-house substrates for gas sensors.

3. Selective sensors produced at Swansea

In recent years four selective sensors have been developed at Swansea. The first is sensitive to the presence of carbon monoxide but shows no response to the lower hydrocarbons methane, ethane, propane and butane (Coles *et al* 1985). This device is produced by sintering an intimate mixture of tin and bismuth oxides. A second sensor exhibits a selectivity opposite to this and is composed of tin dioxide, aluminium silicate and palladium chloride (Coles *et al* 1985). The third, which is essentially composed of the same materials as the first device, is sensitive to the presence of hydrogen but shows little response to the presence of carbon monoxide or lower hydrocarbons (Coles *et al* 1991). The fourth device, which is composed of pure tin dioxide but produced via a novel route, detects the environmentally sensitive gas nitrogen dioxide (NO₂) but is insensitive to any of the previously cited gases (Coles and Williams 1993). The important feature to note with regard to all four sensors is that this selectivity is not produced by temperature control, the sensors exhibiting this behaviour throughout the viable operating temperature range. There will however be an optimum temperature at which the sensors will have maximum sensitivity and

therefore an optimum power at which the substrates should be heated. It is important to remember that the power required to reach a given temperature is predominantly dependent on substrate size and geometry.

As an example the carbon monoxide-selective sensor will be discussed. Figure 5 shows the variation in conductivity with increasing contaminant gas concentration for a CO-selective device in both CO and CH₄. It can be seen that the sensor responds markedly to even low levels of CO whilst the response to CH₄ remains negligible. In fact the response remains negligible well beyond the boundaries of this figure, up to several thousand ppm which for safety reasons were the limits of these tests. The maximum sensitivity is observed at an operating temperature of $\sim 300^{\circ}\text{C}$. As has been previously stated this selectivity is observed over a wide range of temperature. Figure 6 shows the effect of increasing the amount of bismuth oxide in tin dioxide-based sensors sintered at 800°C for 2 h with $\sim 2^{\circ}\text{C}$ per minute furnace heating and cooling. As expected pure tin dioxide responds to both CO and CH₄, but as the amount of Bi₂O₃ is increased the response to CH₄ rapidly diminishes, and above $\sim 16\%$ w/w Bi₂O₃ there is no response to this gas. Conversely, the response to CO remains unaltered up to $\sim 18\%$ Bi₂O₃. Above this level a similar reduction in response is observed, in this case reaching zero at bismuth oxide concentrations in excess of $\sim 23\%$. It can therefore be seen that the ideal composition for this CO-selective device is 17% bismuth oxide with 83% tin dioxide where the response to CO is still at its maximum whilst the response to CH₄ is negligible. This is a curious observation as tin dioxide responds to numerous gases but bismuth oxide is known to show little response as a gas sensor. However, this device is sintered at elevated temperatures and it is therefore important to know what happens to the device under these conditions. Figure 7 shows a series of X-ray diffraction scans for a mixture of

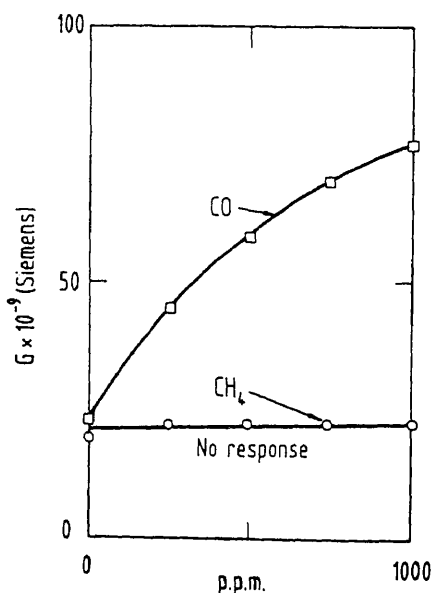


Figure 5. The response of a CO-selective device with increasing gas concentration in atmospheres containing CO and CH₄.

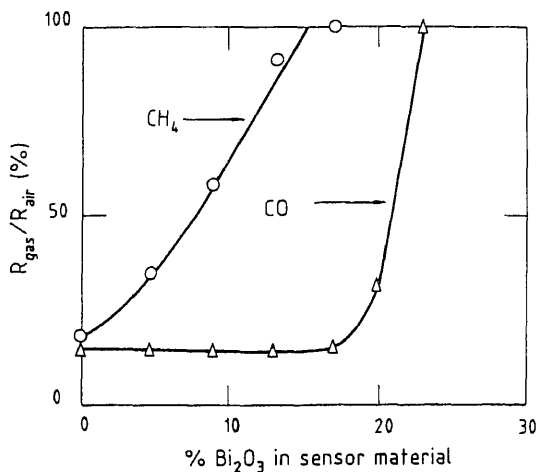


Figure 6. Variation of sensor sensitivity with increasing bismuth oxide content in atmospheres containing 1% CO and CH₄.

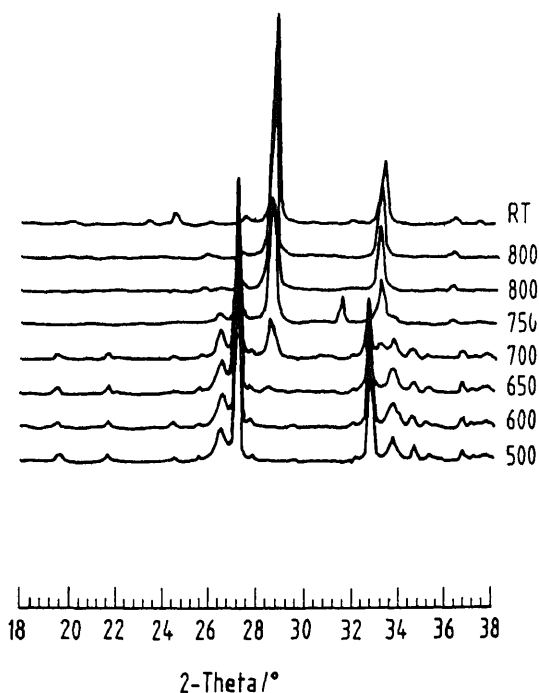


Figure 7. X-ray diffraction patterns from a 2:1 mixture of tin dioxide and bismuth oxide with increasing temperature and after cooling to room temperature.

tin and bismuth oxides with increasing temperature. At temperatures below 600°C the peaks characteristic of these oxides are observed. At temperatures above this a peak is observed at an angle of $2\theta = 28.6^\circ$. This corresponds to the production of bismuth stannate ($\text{Bi}_2\text{Sn}_2\text{O}_7$) (Roth 1956). At 750°C a peak is observed at an angle of

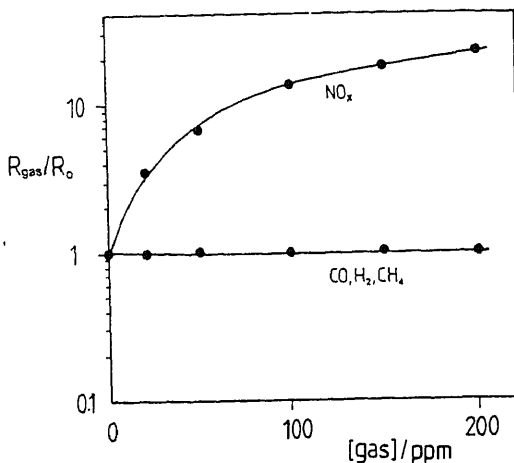


Figure 8. The response of an in-house NO_x sensor with increasing concentrations of NO_2 , CO , CH_4 and H_2 .

$2\theta = 31.4^\circ$ and this represents the phase transition of $\alpha\text{Bi}_2\text{O}_3$ to $\delta\text{Bi}_2\text{O}_3$ which is known to occur at a temperature of $\sim 710^\circ\text{C}$. This peak has disappeared at higher temperatures. It can therefore be concluded that in the actual sensor, after sintering, all of the bismuth oxide has reacted and the sensor is composed of bismuth stannate and excess tin dioxide. The reasons why this material should confer the observed selectivity is unclear but it is known that bismuth stannate has a pyrochlore structure. In fact figure 7 also shows that at elevated temperatures the structure is that of a cubic pyrochlore which becomes a distorted pyrochlore on cooling to room temperature. This crystal form has a very open structure and it has been proposed that it may act as a molecular sieve on the surface of the tin dioxide particles. It should however be noted that evidence for this proposal is inconclusive and attempts to produce similar sensors incorporating other pyrochlore stannates have proved unsuccessful (Coles *et al* 1994).

The most recent sensor to be produced at Swansea selectively detects nitrogen dioxide in the presence of many other fuel and combustion gases (Coles and Williams 1993). This device is produced by depositing a layer of tin directly onto a substrate by radio frequency magnetron sputtering. This layer is then oxidized in air at elevated temperatures by simply powering the substrate heater. Figure 8 shows the response of this device in atmospheres containing NO_2 , CO , CH_4 and H_2 . Clearly this sensor shows a remarkable degree of selectivity for a material that is normally considered to respond to all of these gases. It is hoped that this device may prove useful in monitoring this environmentally sensitive gas in automotive applications such as exhaust monitoring from cars fitted with catalytic converters.

4. Conclusions

There can be no doubt that the world market for sensors of all types will continue to grow. This includes gas sensors that are required to monitor a wide variety of potentially explosive, toxic and environmentally sensitive gases. Although there are

many technologies available for exploitation in this context, and which possess many commercially desirable characteristics, it is clear that semiconductor sensors will continue to hold many advantages over competing devices. At Swansea the problem of selectivity has been the main focus of work for over a decade and four sensors with marked selectivity have been developed. However, there are still many characteristics of these sensors that can be improved, major areas of concern being medium/long-term drift, the ability to produce them reproducibly, and the effects of ambient conditions particularly humidity. These are all problems that are being studied by research groups around the world including our own. Although semiconductor devices have been available commercially for over 20 years there is little doubt that they will continue to form the basis of numerous publications and an integral part of various international conferences for many years to come.

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Magnetic ferroelectric materials

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Abstract. In the form of a succinct overview the structure and symmetry requirements of magnetic ferroelectrics are discussed. Boracites are the best-studied examples and have phases being simultaneously ferroelectric, ferromagnetic and ferroelastic. One of the salient features of such materials is the obligatory occurrence of the linear and bilinear magnetoelectric effects. They represent an invaluable auxiliary information for magnetic symmetry determination by neutron diffraction. Owing to the complexity of property combinations, work with single crystals and polarized light microscopy is obligatory. Key references of the field are given.

Keywords. Ferromagnetic ferroelectrics; antiferromagnetic ferroelectrics; ferroelasticity; magnetoelectric effects.

1. Introduction

In 1994 we celebrate the centennial of Pierre Curie's idea of a material which can be electrically polarized by means of a magnetic field and magnetized by means of an electric field (Curie 1894). There were many unsuccessful attempts of different scientists at finding such an effect (well chronicled by O' Dell 1970). Finally Landau and Lifshitz remarked that time reversal symmetry has to be taken into account and that the magnetoelectric and piezomagnetic effect should be possible in magnetic structures (Landau and Lifshitz 1960). On that basis Dzyaloshinskii predicted the linear magnetoelectric effect to exist in the antiferromagnetic phase (with Shubnikov point symmetry $\bar{3}'m'$) of chromium oxide Cr_2O_3 (Dzyaloshinskii 1959). Shortly thereafter Astrov confirmed the prediction by measuring the electric field-induced magnetization in Cr_2O_3 (Astrov 1960), and the detection of the magnetic field-induced polarization followed step (Folen *et al* 1961; Rado and Folen 1961). These two manifestations of the magnetoelectric effect—measurable in insulators only—can be considered as the two facets of Curie's prediction.

If we take a compensated antiferromagnet like Cr_2O_3 , permitting the linear magnetoelectric effect, we can alternatively say that owing to the magnetoelectric interaction the material becomes a *very weak ferromagnet* under the influence of an electric field and a *very weak ferroelectric* under the influence of a magnetic field. Such a magnetic field-induced ferroelectric is unusual in the sense that its antiferromagnetic domains, which become simultaneously the ferroelectric domains, can be switched by means of an electric field (Martin 1965; Martin and Anderson 1966). We might also speak of an *induced electronic ferroelectric* because in contrast to common ferroelectrics the nuclear structure remains in first approximation immobile and essentially only the spins of the magnetically active unpaired electrons are reversing during the domain switching process.

Independently of the rigorous symmetry approach by Dzyaloshinskii, Smolensky and Ioffe were trying to synthesize ferroelectric ferromagnets by replacing partially

diamagnetic ions by paramagnetic ones on the B-site of oxyoctahedral ferroelectric perovskites. By this approach initially the antiferromagnetic ferroelectric perovskite $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ was synthesized in ceramic form (Smolensky and Ioffe 1958). Later, by studying single crystals, the compound was recognized to have a weak spontaneous magnetic moment in the ferroelectric phase below 9 K (Astrov *et al* 1968). Because of the solid solution approach, implying dilution by diamagnetic ions, the magnetic coupling is, however, substantially reduced.

The simultaneous occurrence of ferroelectricity and (weak) ferromagnetism was first discovered in nickel iodine boracite $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$ (below 61 K) (Ascher *et al* 1966). This compound is a member of a large crystal structure family with the general formula $\text{M}_3\text{B}_7\text{O}_{13}\text{X}$, where M stands for a bivalent cation of Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, etc and X for a monovalent anion like OH^- , F^- , Cl^- , Br^- , I^- , or NO_3^- . Nearly all the boracite compositions with paramagnetic metal ions undergo phase transitions from a cubic high-temperature phase to fully ferroelectric/fully ferroelastic phases (for nomenclature see Aizu 1970), most of which undergo at low temperatures a transition to a (weakly) ferromagnetic phase with orthorhombic, monoclinic or triclinic symmetry (Tolédano *et al* 1985; Rivera *et al* 1985).

2. Conditions for ferromagnetic and antiferromagnetic ferroelectrics

The conditions for the occurrence of ferroelectricity and magnetic order in the same phase—often accompanied by ferroelasticity (for a definition see Aizu 1970)—comprise (i) the presence of adequate structural building blocks, e.g. with double or multiple potential wells permitting ferroelectric-type ionic movements, (ii) magnetic-interaction pathways, usually of the superexchange type, and (iii) the fulfilment of symmetry conditions (Schmid 1973; Ascher 1973; Freeman and Schmid 1975).

Among the 122 Shubnikov–Heesch point groups there are 31 allowing a spontaneous magnetization and 31 allowing a spontaneous polarization. However, the occurrence of both ferro(i)magnetism and ferroelectricity in the same phase is permitted in 13 point groups only (Ascher 1973; Schmid 1973). The presence of both ferroelectricity and antiferromagnetism is allowed in 8 point groups (Schmid 1973); however, this number increases drastically when the possible symmetries of incommensurate phases are included.

For symmetry reasons all ferro(i)electric ferromagnets allow *a fortiori* the linear and both bilinear (in the electric field and the magnetic field) type magnetoelectric effects (Ascher 1968; Schmid 1973; Freeman and Schmid 1975). In the boracite family the linear and bilinear (in the magnetic field) magnetoelectric effect has been measured for a variety of compositions (for a bibliography see: Burzo 1994).

For those ferromagnetic ferroelectrics which are simultaneously ferroelastic, a coupling between the spontaneous polarization, spontaneous magnetization and spontaneous deformation is possible. Such a coupling has for the first time been demonstrated for $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$ (Ascher *et al* 1966), in which an electric field-induced 180° reversal of the spontaneous polarization causes a symmetry-conditioned 90° reorientation of the spontaneous magnetization, and a magnetic field-induced 90° reorientation of the spontaneous magnetization causes a 180° reversal of the spontaneous polarization. Such coupling between the spontaneous polarization and the spontaneous magnetization requires ferroelasticity to be allowed and leads to nonlinear effects with hysteresis cycles and memory behaviour, whereas the linear and bilinear (special

case: quadratic) magnetoelectric effects are in principle non-lossy, thermodynamically reversible effects, if domain switching and possible relaxation phenomena are disregarded.

3. Examples of ferromagnetic and antiferromagnetic ferroelectrics

The simultaneous occurrence of ferroelectricity and ferromagnetism has reliably been proved in the boracite family (Tolédano *et al* 1985) and recently in the phosphate KNiPO_4 (Lujan *et al* 1994). The new family of perovskite–orthoferrite solid solutions, $\text{Bi}_{1-x}\text{RE}_x\text{FeO}_3$ ($\text{RE} = \text{La}, \text{Dy}, \text{Gd}$), with pyroelectric, ferrimagnetic, magnetoelectric phases and Curie temperatures above room temperature, are very promising (Gabbasova *et al* 1991).

Ferroelectric antiferromagnets like BiFeO_3 , BaMnF_4 , REMnO_3 ($\text{RE} = \text{rare earth}$), etc are more frequent (Schmid 1973; Freeman and Schmid 1975). It is noteworthy that in BiFeO_3 and BaMnF_4 the linear magnetoelectric effect cancels because of incommensurate structures (Tabares-Munoz *et al* 1984; Sciau *et al* 1990). As a consequence the magnetoelectric behaviour was found to be only that of a non-centrosymmetric paramagnet, as manifested by the bilinear (in the magnetic field) magnetoelectric effect (Tabares-Munoz 1984; Sciau *et al* 1990). In the large perovskite family many compositions are potential magnetic ferroelectrics (Venetsev and Gagulin 1994). However, these materials, often known in ceramic form only, are hardly investigated. There is a reason for that: in perovskites and other compounds with a cubic high-temperature prototypic point symmetry $m\bar{3}m1'$ the number of domain states may climb up to 96 for a triclinic ferroelectric ferromagnetic or antiferromagnetic phase. Therefore, when studying such complex ferroelectric magnetics, reliable physical measurements necessitate the availability of single crystals and the preparation of single-domain specimens in conjunction with the indispensable visual control of the domain state by low-temperature and high-temperature polarized light microscopy, both in transmitted and reflected light (Schmid 1993). There is great paucity of such investigations on single crystals of perovskites and other materials up to now.

4. Applications of the magnetoelectric effect

One of the important applications of the linear and higher-order magnetoelectric effects, occurring in magnetic ferroelectrics, resides in the fact that they give us precious auxiliary information for determining the magnetic point group, and herewith the magnetic space group, because the Schönflies–Federov space group is usually known from X-ray diffraction work. This means that they provide a precious complementary tool for neutron diffraction, which seldom allows us to determine the magnetic point and space group unequivocally.

Other important scientific applications of the magnetoelectric effect are the accurate determination of magnetic phase-transition temperatures and critical exponents; the study, switching and ‘poling’ of antiferromagnetic domains by means of simultaneous application of magnetic and electric fields; the study of defects in magnetic phases; magnetic and electric field-induced phase transitions (e.g. spin-flop and metamagnetic transitions); etc (Freeman and Schmid 1975; Schmid *et al* 1994).

5. Conclusions

In the Proceedings of the 2nd International Conference on Magnetoelectric Interaction Phenomena in Crystals (Schmid *et al* 1994), the reader will find more information on magnetic ferroelectrics, related materials, their properties, and in particular on theory and experiment of the magnetoelectric effect. This effect represents one of the most salient features of magnetic ferroelectrics.

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Studies of diamond-like carbon films prepared by ion beam-assisted deposition

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Abstract. Ion beam-assisted deposition offers a novel and unique process to prepare diamond-like carbon (DLC) films at room temperature, with particularly good interface adhesion. This advantage was explored in this study to deposit highly wear-resistant coating on bearing 52100 steel. Both dual ion beam sputtering and ion beam deposition were employed. Various bombarding species and energy were investigated to optimize the process. Raman, X-ray photoelectron and Auger electron spectroscopy were used to characterize the bonding structure of DLC. Extensive experiments were carried out to examine the tribological behaviour of the DLC/52100 system. A metal intermediate layer can help tremendously in wear resistance. The results are optimistic and may lead to useful applications.

Keywords. Diamond-like carbon films; ion-beam assisted deposition.

1. Introduction

Diamond has many unique properties. High hardness—diamond is number one on the Mohs scale—is one of the most notable. Scientists have been trying to make diamond artificially for many years. Bundy of General Electric achieved it in 1954, by using high temperature and super high pressure with Ni catalyst (Bundy 1955). Since then a number of attempts have been made to prepare diamond by chemical vapour deposition (CVD) decomposition of hydrocarbons and CCl_4 on diamond seeds (Spitsyn *et al* 1988). Deryagin *et al* (1976) first reported success in preparing diamond by CVD on nondiamond substrates. This work stimulated an avalanche of research on studies of low-temperature and low-pressure preparation of diamond, and new methods and approaches increasingly emerged.

A number of factors affect the formation and properties of these low-temperature low-pressure diamonds, such as gas composition, temperature, substrates, etc. There is also the problem of adhesion at the interface. Many of the prevailing methods employ rather high substrate temperatures (e.g. 800–1000°C) and are quite particular of the substrates themselves. Among all the existing methods ion beam-assisted deposition (IBAD) is probably the one that uses the lowest temperature (room temperature) and can be applied to any substrate. Of course, it is also probably the method furthest from the equilibrium state of diamond. Therefore, so far only diamond-like carbon (DLC) films can be obtained (see figure 1). However, these DLC can be optimized to have excellent properties and to have important potential applications. In fact they even possess some advantageous aspects compared to diamond. This constitutes the motivation of our research programme.

2. IBAD and the equipment

IBAD is a new version of ion implantation. Figure 2 is a schematic diagram to show the difference. It maintains the advantage of the useful energy carried by the charged ions and adds the advantage of building up of an overlayer.

The energy of ion beams is a very useful tool to enhance chemical reactions. With this in mind, we have synthesized 17 metallic nitrides at room temperature since 1980 (Li 1986). The energetic ions can induce an avalanche of primary and secondary

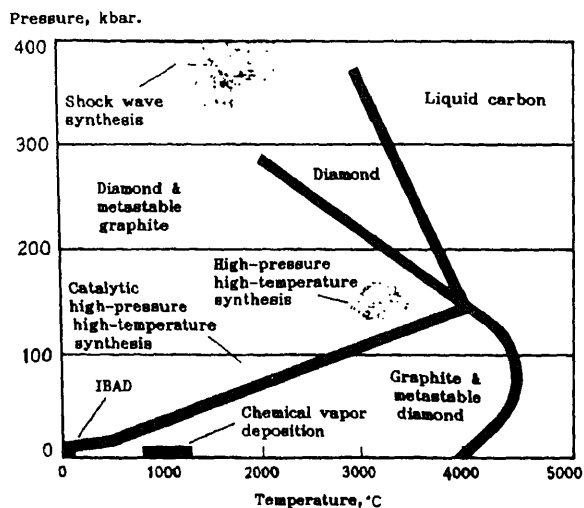


Figure 1. T-P phase diagram of carbon.

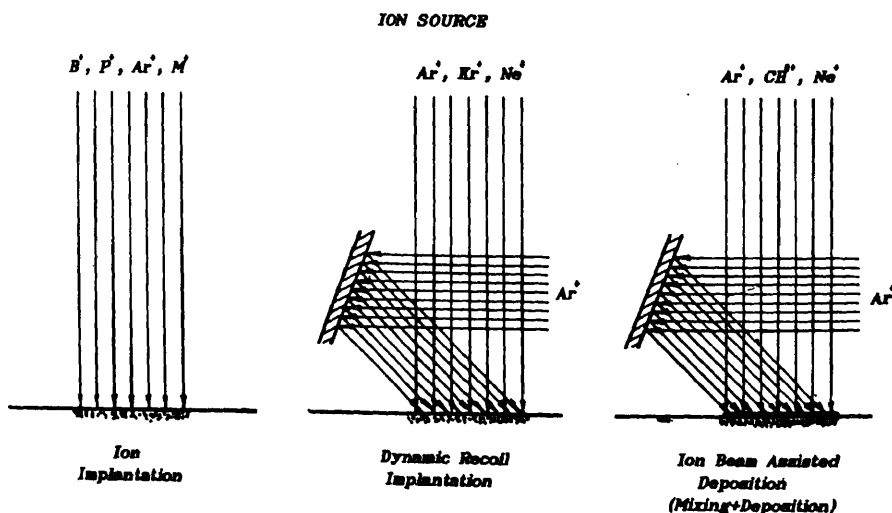


Figure 2. Schematic diagram of ion implantation, dynamic recoil implantation and ion beam assisted deposition (IBAD).

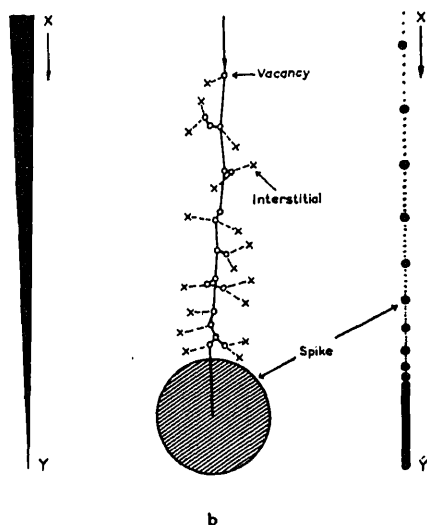
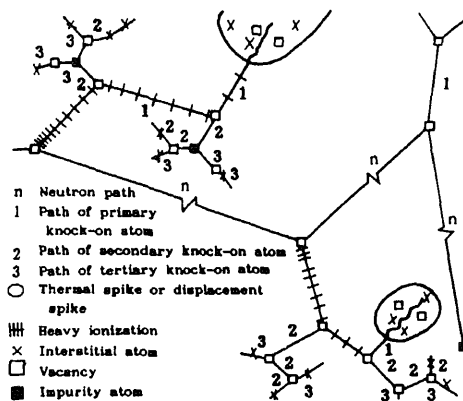
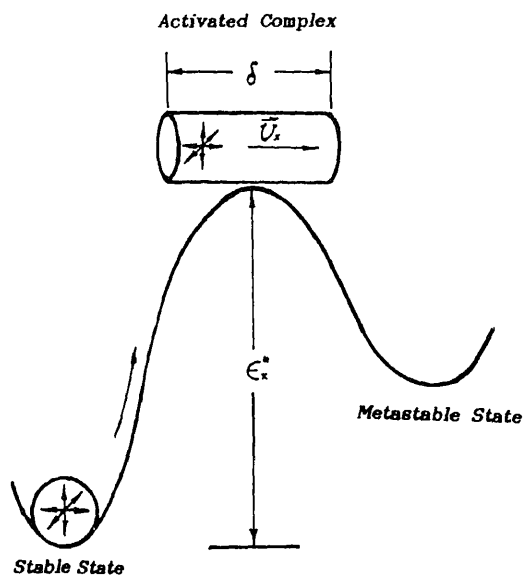


Figure 3. a. Collision cascade induced by an energetic particle and b. thermal spikes and displacement spikes.

recoil atoms whose kinetic energy (say 100 eV) can easily surpass the required reaction activation energy (0.5 eV) (figure 3a). Furthermore a series of thermal spikes and displacement spikes can be created on the paths of their trajectories (figure 3b). The temperature of the spike is estimated to be about 3800 K and the duration about 10^{-11} sec (Weissmantel *et al* 1980). Therefore the requirements of a chemical reaction can be satisfied both energy-wise and time-wise. This process, which we label 'collision-activated reaction', can bring a high-temperature process to room temperature (see figure 4).

The energetic ions serve another important function, i.e. to cause an interface mixing. Figure 5 is a simulated picture to illustrate this point. This ion-mixing process can sometimes form new phases in the region. This effect can generally lead to high interfacial adherence. In this case, it offers the potential to obtain a 'coherent' interface,



ϵ^* 10 kJ/mol; 0.5 eV;

$\vec{U}_x$ X-component of atomic velocities along
the direction of translation;

δ Activation length;

$\tau = \delta / \vec{U}_x \sim 10^{-14}$ s.

Figure 4. Energy associated with the impinging particle can bring the state from stable to metastable. The collision-activated complex has a long enough lifetime.

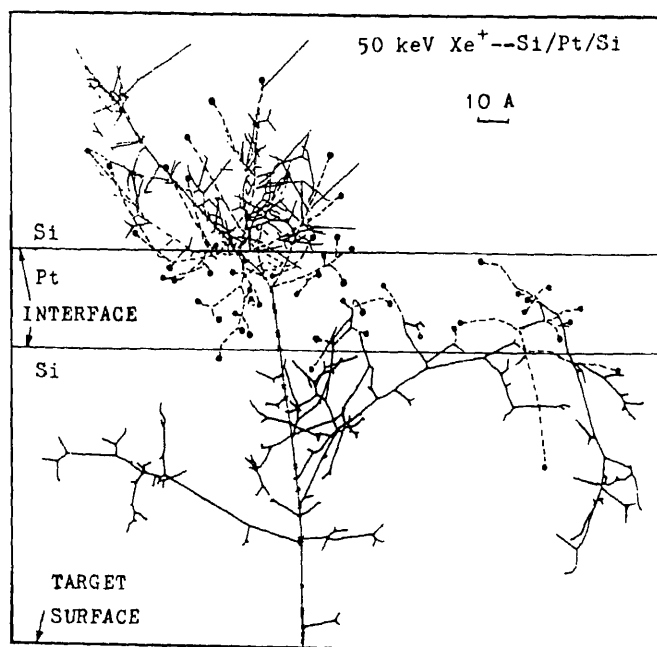


Figure 5. An energetic particle-induced interface mixing (a computer simulation).

not relying on epitaxial growth but on interfacial mixed bonding. Lattice misfit is no longer a problem.

To sum up, it may be stated that a low-temperature (room temperature) process, a strong interfacial adhesion, and the freedom in choice of substrates are the unique advantages of the IBAD route for preparation of many surface coatings, including DLC films.

The IBAD system used for the present studies was developed in 1990 in this laboratory. Figure 6 is a schematic diagram of it. Three Kaufmann ion sources are available. The source labelled 7 is a specially designed high-density source used for sputtering with generally a voltage of 2–4 kV and a current of 100–150 mA. Source 1 is for high-energy bombardment, with voltage from 3 kV to 40 kV. Source 8 is for low-energy bombardment with voltage from 100 to 700 V. The part labelled 2 is a rotatable target holder, water cooled. Four targets can be attached. This number of targets together with a variation of ion species for bombardment can bring about many different combinations. Part 6 is a water-cooled specimen holder; it may be water-cooled or heated up to 400°C. The vacuum system consists of a set of mechanical and diffusion pumps to make a base pressure of about 2×10^{-4} Pa. Such an IBAD system proves to be quite versatile, and not only offers a great number of possibilities for film composition, from single element to various alloys and compounds, but also for ordinary sputtering or ion-assisted sputtering from ions from 100 eV to 40 keV.

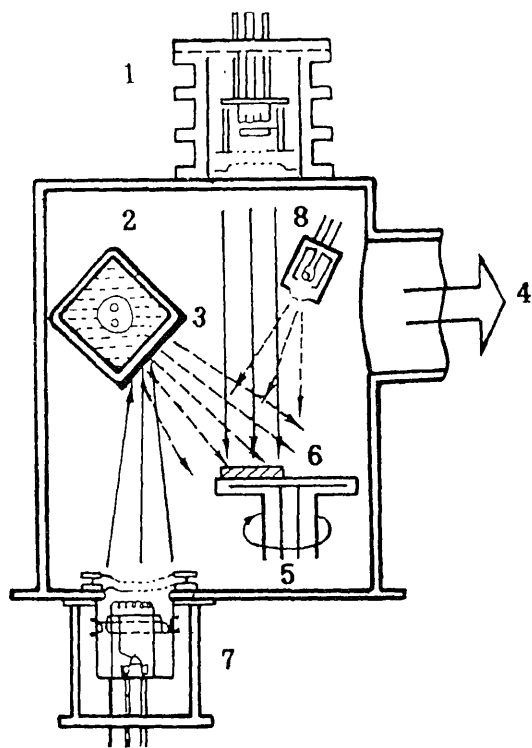


Figure 6. A schematic diagram of the IBAD system. 1. Medium energy ion source, 2. four-fold rotatable target holder, 3. target, 4. vacuum system, 5. rotatable sample holder, 6. substrate, 7. sputtering ion source for deposition and 8. low energy ion source.

To study DLC deposition with the above equipment, both ion beam deposition (IBD) and dual ion beam sputtering (DIBS) were used. Table 1 shows the schemes so far experimented. The process parameters involve direct deposition or deposition by sputtering, the carbon source with or without H_2 , bombarding energy from 100 eV to 25 keV, the species, such as Ar^+ , Ne^+ , N^+ and CH^{n+} , the substrate materials, e.g. Si(111) wafer, glass, NaCl, AISI 52100 steel, etc.

4. The microstructure

The appearance of the DLC films, as pictured by SEM, is always of a very smooth and flat surface, as shown in figure 7, the featureless morphology is typical of amorphous carbon. Roughness of the substrate can be somewhat improved after

Table 1. The IBAD experimental scheme.

	Sputtering	Bombarding species
DIBS	Graphite target	Ar^+ , Ne^+ , CH^{n+} , N^+
	Ar^+ sputtering	$Ne^+ + CH^{n+}$ ($Ne^+/CH^{n+} = 1$)
	3–3.5 keV, 100–150 mA	$N^+ + CH^{n+}$
IBD		CH^{n+}
		$CH^{n+} + Ne^+$
		$N^+ + CH^{n+}$

Substrates: Si(111), NaCl, WC, 52100.

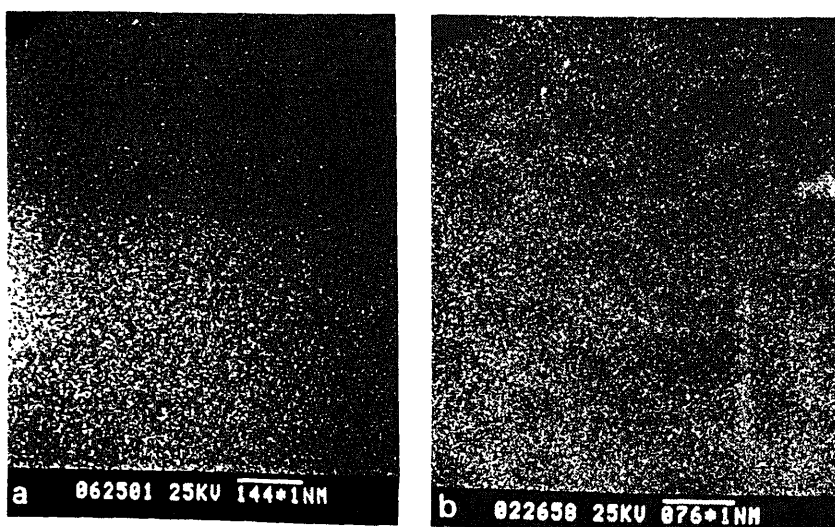


Figure 7. SEM photographs of DLC films prepared by (a) 200 eV and (b) 15 keV CH^{n+} bombardment.

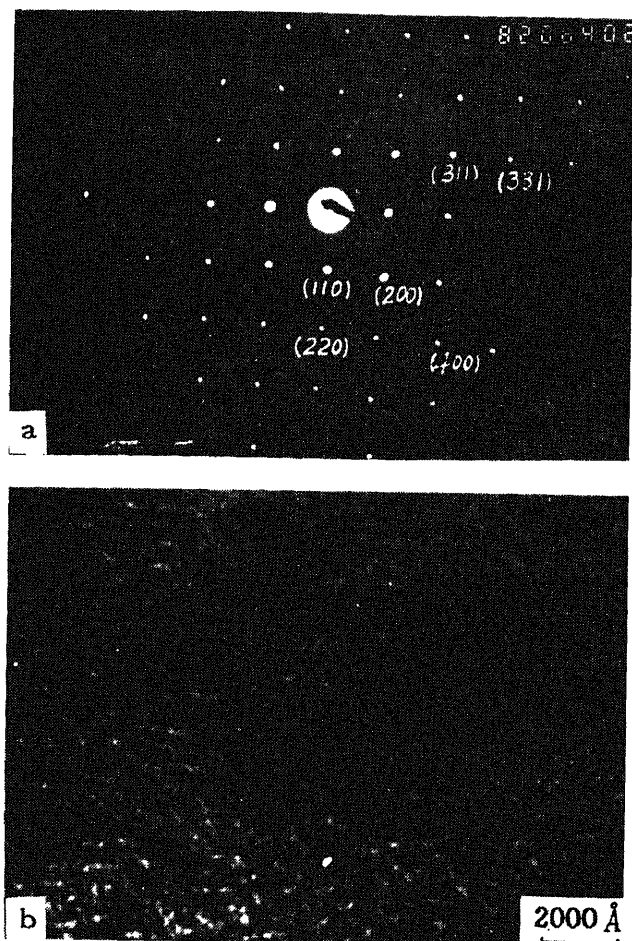


Figure 8. (a) Selected-area diffraction of DLC films and (b) TEM image of surface morphology.

deposition; R_a (roughness average) decreased from $0.024\ \mu\text{m}$ to $0.016\ \mu\text{m}$ in one case. This smoothness of coating is considered to be a useful characteristic of the DLC films. Figure 8a shows the diffraction spots of some crystals dispersed on amorphous matrix of DLC films, as seen in figure 8b. Their spacings are identified to be 2.57, 1.89, 1.34, 1.2 and $0.94\ \text{\AA}$; for comparison, those of cubic diamond: $d(110) = 2.52$, $d(200) = 1.78$, $d(210) = 1.26$, $d(311) = 1.08$ and $d(400) = 0.89\ \text{\AA}$ (Min *et al* 1992). Therefore some of the films clearly contain dispersed diamond particles.

Thickness of the film generally used is over 600 nm as calculated from the Rutherford backscattering (RBS) spectra, such as shown by figure 9.

The composition corresponding to figures 7 and 8 was determined by Auger electron spectroscopy (AES) (figure 10). Some oxygen appears on the surface but after 3 min r^+ sputtering etching at 1 keV, the films show only carbon atoms.

However, in the cases when hydrocarbons are employed, no attempts have been

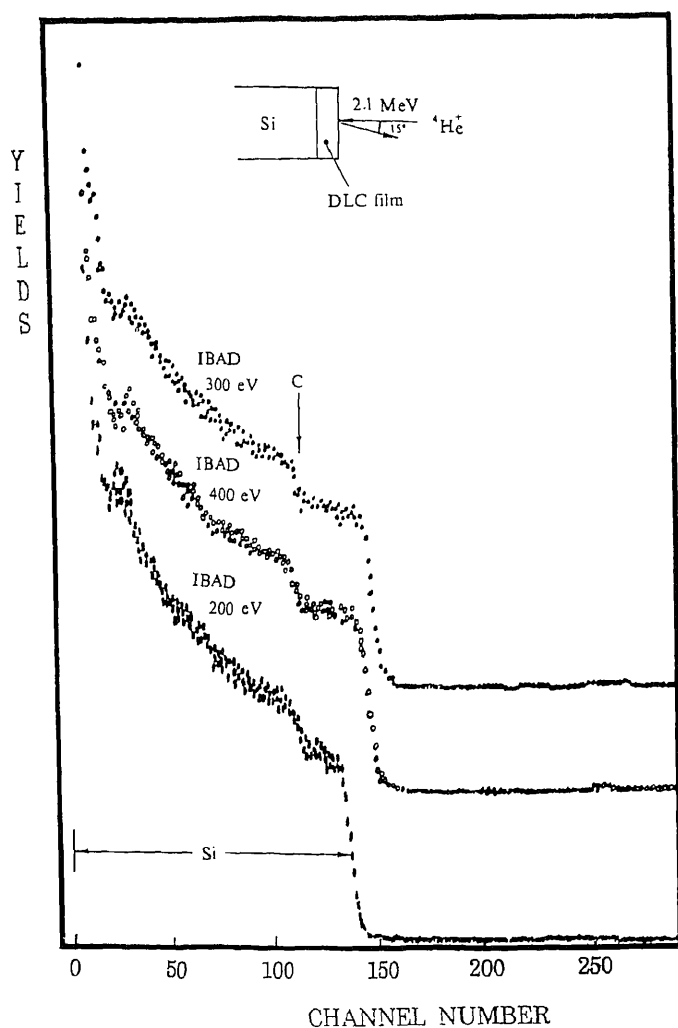


Figure 9. RBS spectra of synthesized DLC films.

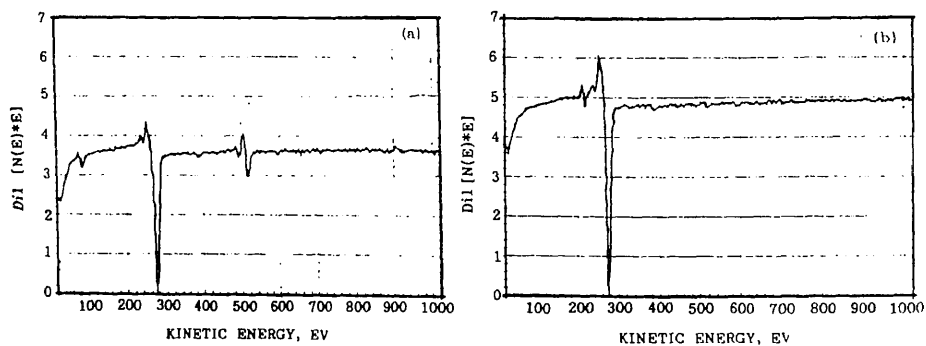


Figure 10. AES of carbon films prepared by IBAD: (a) surface spectrum, (b) spectrum after sputtering 3 min at 1 keV.

Bonding in DLCs

The nature of bonding in DLC has been investigated using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and AES.

Typical AES spectra of diamond, graphite and DLC are shown together for comparison in figure 11a (Moravec and Orent 1981). The most distinguishable feature of the diamond AES fine structure from that of graphite is the shoulder at the right (higher energy) side of the 250 eV peaks. The diamond shoulder goes up while the graphite shoulder goes down, and in DLC the shoulder is in between.

Figures 11b and c show the AES features of DLC prepared in the present study. It is clearly seen in all cases that the AES spectrum resembles the diamond spectrum more as the bombarding energy gradually decreases; 200 to 400 eV bombardment appears to offer the best result. It is also noticed that the trough (actually the peak point of the carbon KLL AES electrons) shifts gradually to higher energy as the bombarding energy decreases; so is the trend of the 250 eV peaks. All these features could be taken as an indication that more sp^3 bonds are formed when the ion beam energy is around 200 eV.

Stronger evidence of this phenomenon can also be observed in the Raman spectra (figures 12a and b, where the 1333 cm^{-1} peak becomes obvious also for a bombarding energy of 200–400 eV).

The XPS spectra point to similar trends (figure 13). There are three distinct spectral regions in the valence band of natural diamond (figure 13a) (Mizokawa *et al* 1987). Region I has a peak between 16 and 21 eV which arises from s -like bonds, region II has a peak between 10 and 15 eV representing the mixture of s and p characters, region III between 3 and 10 eV is attributable to the p bonds (Mizokawa *et al* 1987). Figures 13b and c show the spectra of DLC prepared by DIBS and IBD processes. Again, around 200–400 eV, the s - p mixed bond comes to be more prominent. Figure 14 shows the change of C1s peak positions of DLC films prepared by IBD with bombarding energy between 15 keV and 200 eV. It is very clear that as the energy is reduced from 15 keV to 200 eV, the binding energy comes closest to that of pure diamond, 285.05 eV.

All the above spectra lead to an understanding of the structure of the DLC films. They are amorphous, but their content of sp^3 bonds may be increased by low-energy-

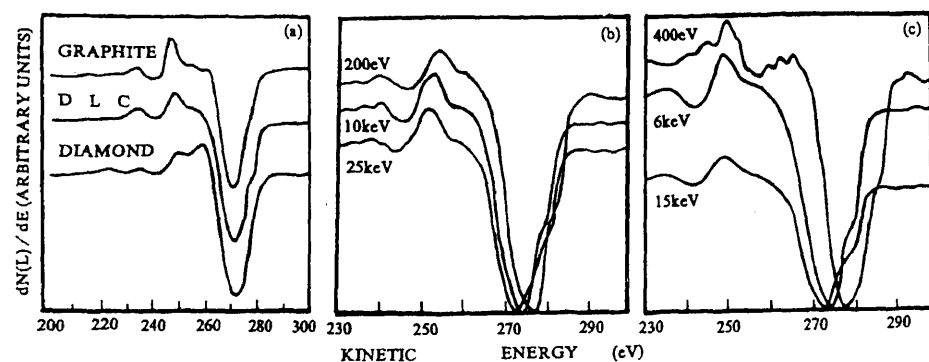


Figure 11. (a) AES of diamond, graphite, and typical DLC film, (b & c) AES of DLC films prepared by DIBS (b) and IBD (c) both at different energies.

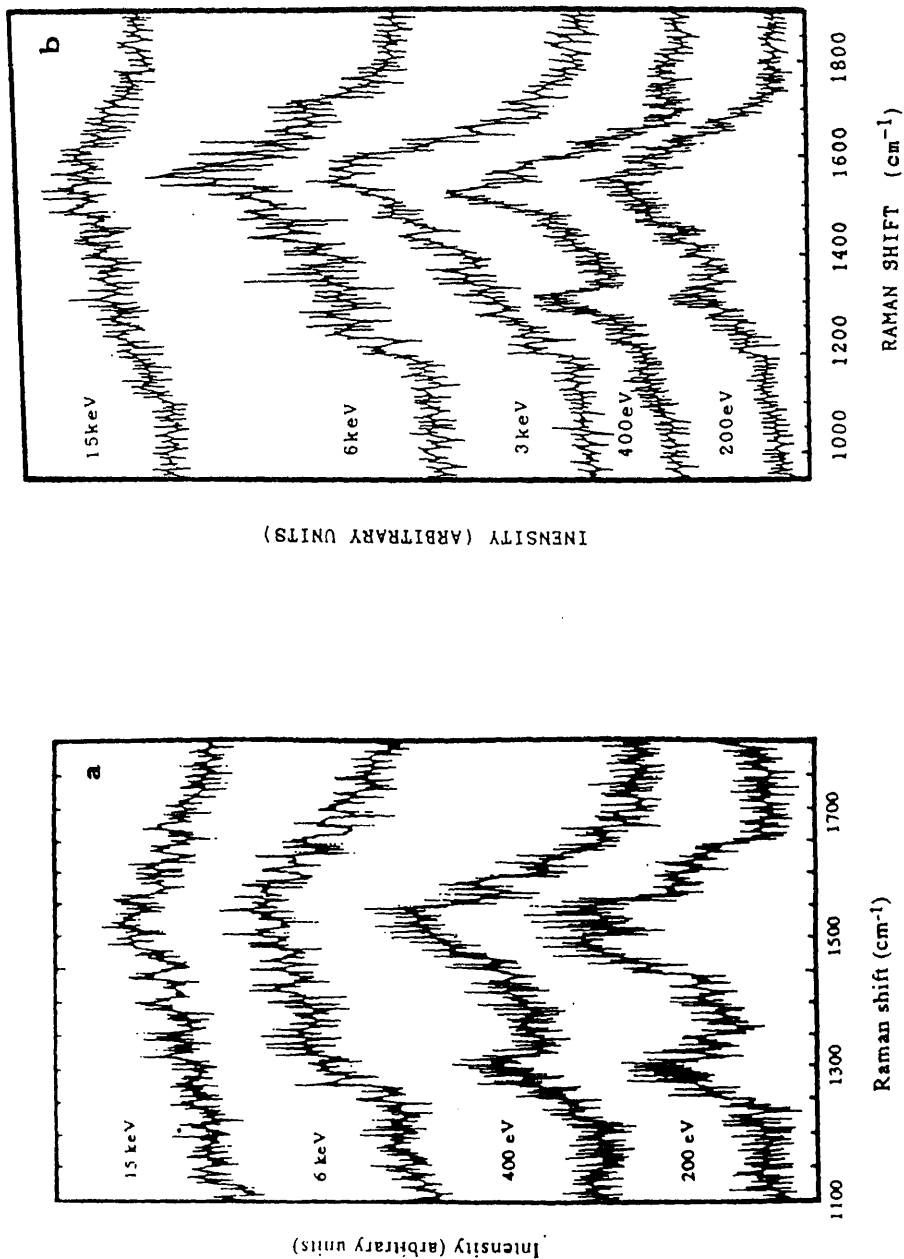


Figure 12. Raman spectra of DLC films prepared by (a) DIBS and (b) IBD at various CH_4^+ bombarding energies.

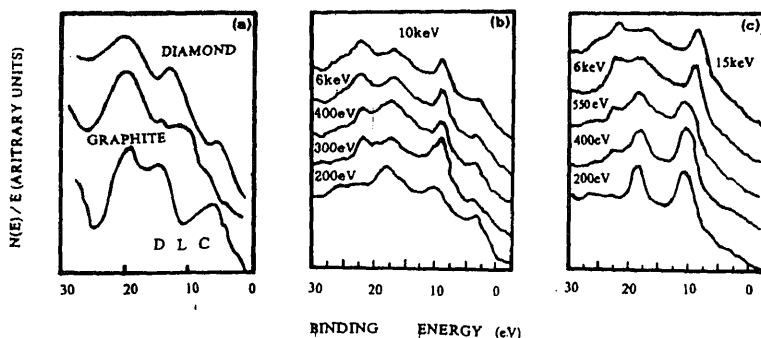


Figure 13. (a) XPS of diamond, graphite, and typical DLC film, (b & c) XPS of DLC films prepared by DIBS (b) and IBD (c) both at different energies.

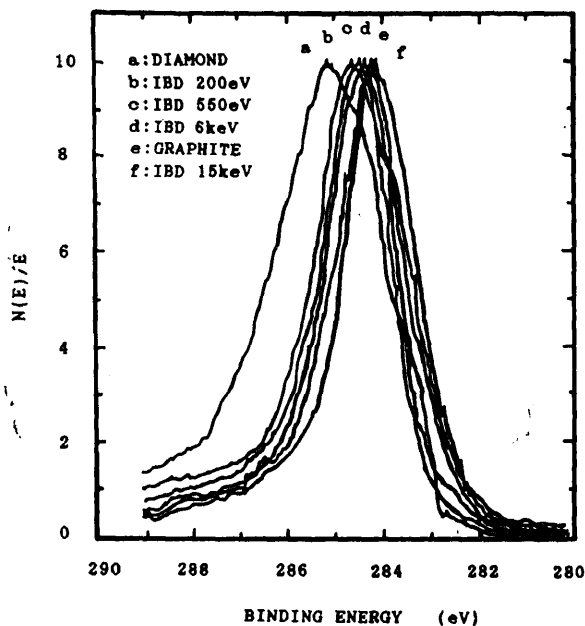


Figure 14. The main C1s peaks of diamond, graphite and DLC films prepared by IBD.

assisted deposition, i.e. they tend to be more diamond-like to a certain degree under certain processing conditions. With Ne^+ bombardment, dispersed diamond crystals can be present (see figure 8).

6. Hardness of DLC and the bombarding energy

Hardness is one of the properties of DLC that one is most concerned with. Table 2 shows the results of the measurements.

Two things are pointed out by these data. Between 3 keV and 25 keV bombarding energy the hardness is not quite high and is not sensitive to energy variation. However,

Table 2. Hardness (kgf/mm^2) of DLC films bombarded by CH^n+ under different energies (substrate: Si(111)).

Bombarding energy (eV)	200	300	400	550	3000	6000	10000	15000	25000
DIBS	10 g				1550	1630	2180	1560	1600
	20 g	5100	3250	2720					
IBD	10 g	3000		3500	2700	1395	1290	1550	1450

Table 3. Hardness (kgf/mm^2) of DLC films synthesized under different ion bombardments (substrate: Si(111)).

Bombarding energy (eV)	200			400	
Bombarding ions	Ne^+	$\text{CH}^n+ + \text{Ne}^+$	$\text{CH}^n+ + \text{Ne}^+ + \text{Ar}^+$	CH^n+	N^+
Ratio of gas pressure	1	1:1	2:1:1	1	1
Knoop hardness 10 g	4010	4540	4300	3500	5260*

* The substrate is the disc of WC.

at 200–550 eV, the hardness has much higher values, particularly in the case of $\text{Ar}^+ - \text{CH}^n+$ DIBS, where the highest value is reached at 200 eV bombardment.

Table 3 shows the hardness of the DLC films synthesized under different ion bombardments. It indicates that DLC films with 200–400 eV ion-assisted bombardment usually have high hardness of 3500–5000 kgf/mm^2 .

The high hardness in the 200–400 eV range of bombarding energy obviously is connected to the bonding structure of the films as discussed in the previous section.

7. Tribological properties

For practical mechanical applications one has to examine the actual tribological behaviour of the DLC films and some other important properties. Two schemes of tribological measurements were made. They are illustrated by figures 15 and 16.

Figure 15 shows a reciprocal version. The wear track created has a length of 2 mm. With a ball of 9.5 mm in diameter, it is estimated that a load of 2 N corresponds to a contact stress of 0.8 GPa. Most previous measurements (Braum 1989; Kobs *et al* 1991; Ochsner *et al* 1991; Bhattacharya *et al* 1991) have been made under 1 or 2 N loads. For actual bearing operations, however, the contact stress may be up to 3–5 GPa. Therefore the tribological behaviour of DLC films under larger loading should be pursued. AISI 52100 steel is used for the substrate to simulate practical combination. Load employed ranged between 2 and 30 N, corresponding to contact stress of 0.8–2.15 GPa. During the wearing process, the friction coefficient can be

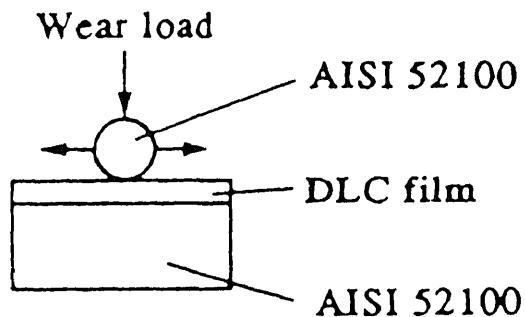


Figure 15. A schematic diagram of the reciprocal ball on disc tribometer. Motion, back and forth; stroke, 2 mm; frequency, 10 Hz; ball diam. 9.5 mm; disc diam. 28 mm; disc thickness 2 mm.

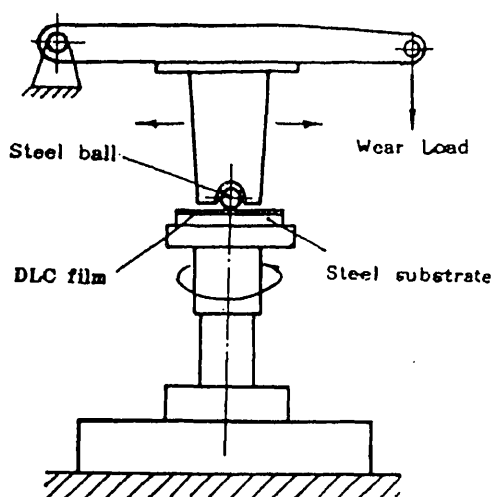


Figure 16. A schematic diagram of the revolving tribometer.

Table 4. Wear properties of DLC films under different wear loads*.

Load (N)	2	5	10	15	20	30
Sliding distance (m)	72	72	72	60	48	12
Groove wear volume ($\times 10^6 \text{ mm}^3$)	7.52	219.59	409.71	556.6	706.48	2733.02
Wear coeff. ($K \times 10^6$)	0.94	10.98	10.24	11.132	13.25	136.65
AWN	6.02	4.959	4.99	4.95	4.87	3.86

* All tests were carried out at a temperature of about 27°C and relative humidity of 50%.

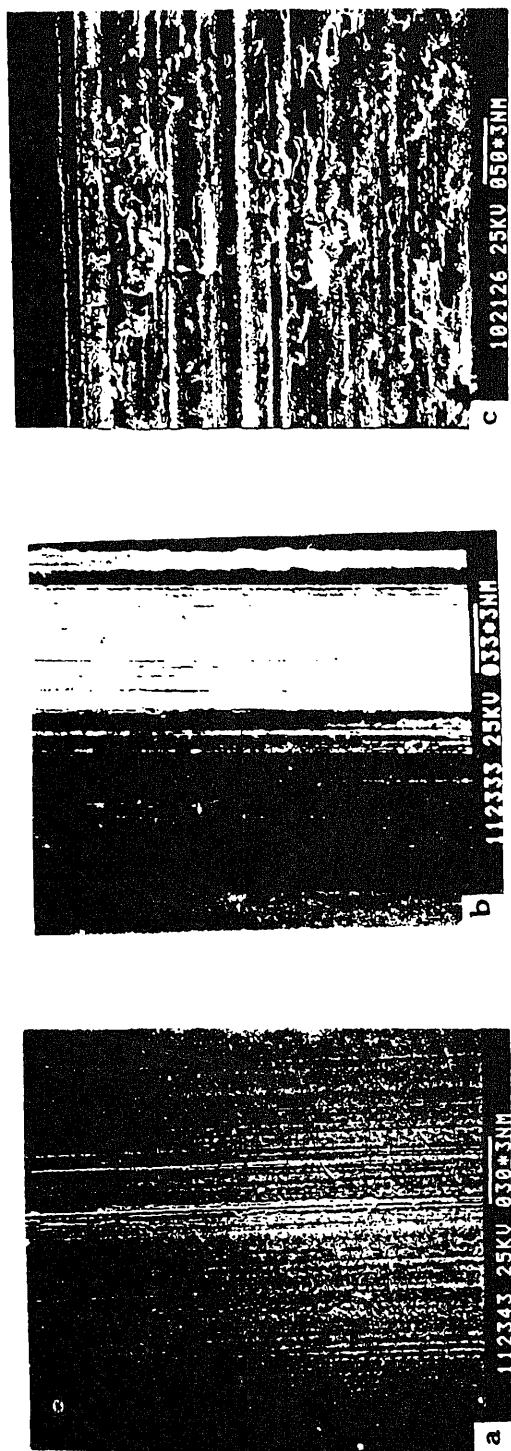


Figure 17. SEM micrographs of wear tracks produced by a steel ball sliding with a wear load of (a) 5 N, 30 min; (b) 15 N, 25 min; (c) 30 N, 10 min.

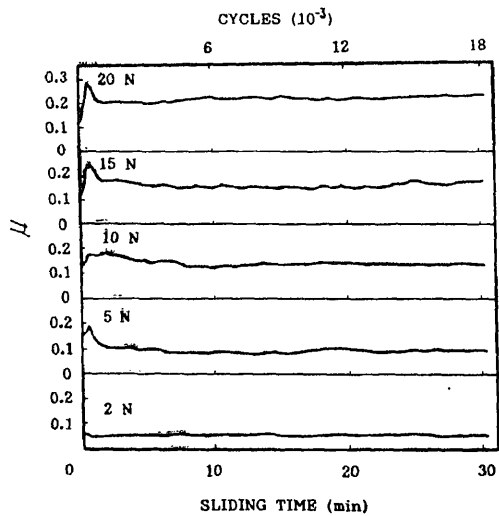


Figure 18. Friction coefficient vs sliding time for loads of 2 N, 5 N, 10 N, 15 N and 20 N for DLC films deposited on the 52100 steel.

monitored and evaluated on a chart recorder as a function of wearing time. Volumetric wear can be measured and calculated to offer two parameters for evaluation, i.e.

$$\text{wear coefficient: } K = (\delta V H_k) / (SP)$$

$$\text{anti wear number: } AWN = -\log K.$$

Here δV is volumetric wear, H_k is knoop hardness, S is distance travelled, and P is wear load.

Results for IBD DLC deposited with an energy of 200 eV are shown in table 4. SEM pictures of the tracks are shown in figure 17, the coefficient of friction in figure 18.

The data lead to the following facts: The coefficient of friction of DLC under 2 N is very low, only 0.05. Even at a very high load of 20 N, the coefficient of friction only goes up to 0.2. This is much lower than the value of 0.75 for AISI 52100 steel. The surface is only slightly scratched after wearing under a load of 5 N after 30 min (figure 17a). The wear track in the case of load of 2 N is too shallow to be shown under SEM and the wear coefficient is two orders less than in the other tests shown in table 4, and AWN is roughly double that under 30 N. This proves that hard DLC film has a strong wear-resistance under a load of 2 N and a steady wearing can proceed for a long time without lubrication. An important fact should be pointed out that AWNs do not change much between 5 and 15 N loads. For the case of 15 N, which represents a very severe test, the coefficient of friction can still remain quite low (0.15) even when the substrate starts to expose itself. This low friction coefficient may originate from the sp^2 component of bonding in the film and effectively reduce the wear rate. Therefore the presence of sp^2 could be an advantageous aspect for the tribological applications of DLC films (Braum 1989; Miyake and Kaneko 1991).

DIBS offer similar results. Figure 19 gives the relationship of friction coefficient against load, up to 56 N, at which the wear carries entirely on the 52100 substrates.

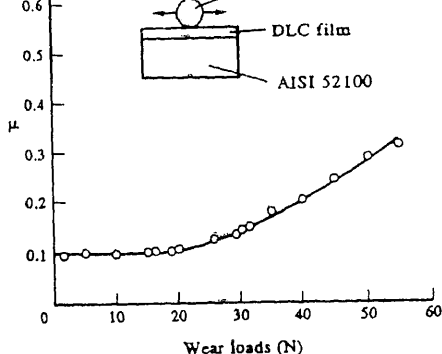


Figure 19. Friction coefficient values for DLC films as a function of increasing wear load.

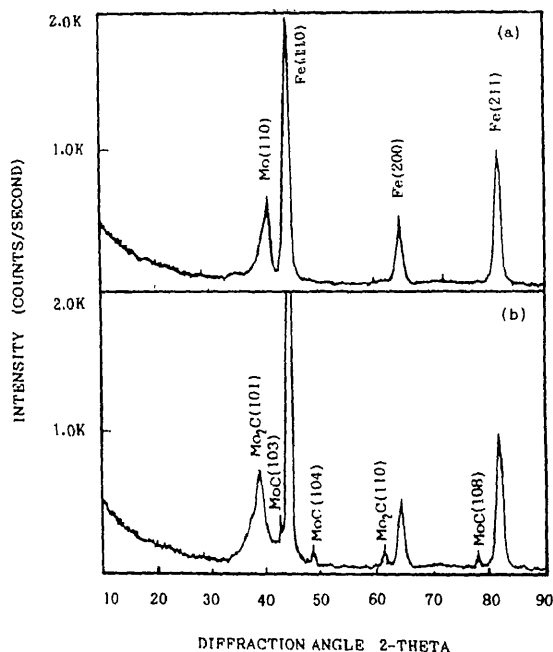


Figure 20. X-ray diffraction patterns of (a) Mo film and (b) DLC/Mo film on AISI 52100 steel.

8. Dynamic mixing in interlayer interfaces on tribological enhancement

Amorphous DLC films with low friction coefficients are very suitable for applications in mechanical devices. However, the adhesion of DLC films often decreases with increasing thickness of DLC films deposited on AISI 52100 steel. This limits DLC films to use as wear-proof coating under heavy load condition. In order to enhance

the adhesion of DLC film to steel substrate, a thin metal film such as molybdenum (Mo) was first prepared on the steel substrate and then DLC films deposited on it. Prior to deposition, atomic mixing was carried out by Ar^+ -sputtering a pure Mo plate to deposit Mo atoms on the substrate with simultaneous bombardment by 35 keV and $25.5 \mu\text{A}/\text{cm}^2$ Ar^+ to create a wide atomic mixing band of Mo/Fe around film/substrate interface. Similarly a wide intermixed DLC/Mo interface was then fabricated by sputtering a high-density graphite target with other conditions identical to those in the formation of the above atomic-intermixed Mo/Fe interface.

The X-ray diffraction patterns of DLC/Mo/steel substrate are shown in figure 20, and the element concentration profiles around both Mo/Fe and DLC/Mo interfaces are depicted in figure 21. It is obvious that due to high-energy Ar^+ bombardment, significant atomic intermixing occurred in both Mo/Fe and DLC/Mo interfaces (figure 21) and the molybdenum carbides, MoC and Mo_2C , were formed in the DLC/Mo interfaces (figure 20). These metallic compounds are very effective in hindering the diffusion of carbon atoms into steel substrates (as seen in figure 21). The existence of the molybdenum carbides and the atomic intermixing at both Fe/Mo and Mo/DLC interfaces would greatly enhance the adhesion of DLC films to steel substrate and prevent DLC films from exfoliation in application.

The coefficients of friction as a function of the wear time under different wear loads are depicted in figure 22. It is notable that even when the wear load increases to 25 N, the coefficient still remains in the range 0.06–0.14, which is much less than that in current literature (Raveh *et al* 1993).

The typical morphology of the wear groove is shown in figure 23. As the wear load was increased from 2 N to 25 N, the worn grooves on DLC films were still quite even and flat, and no exfoliation occurred. This demonstrates that the DLC film has very good adhesion to Mo/steel substrate.

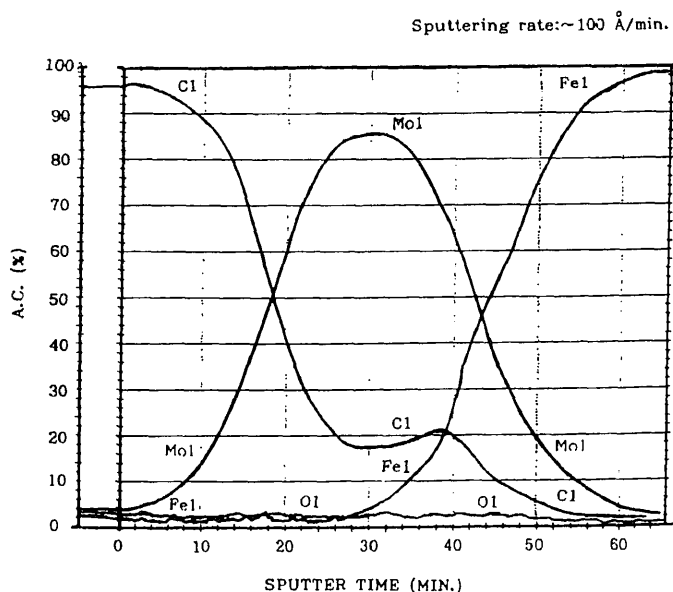


Figure 21. The sputter-etching curve of AES in the atomic mixing area around DLC/Mo/AISI 52100 steel interfaces.

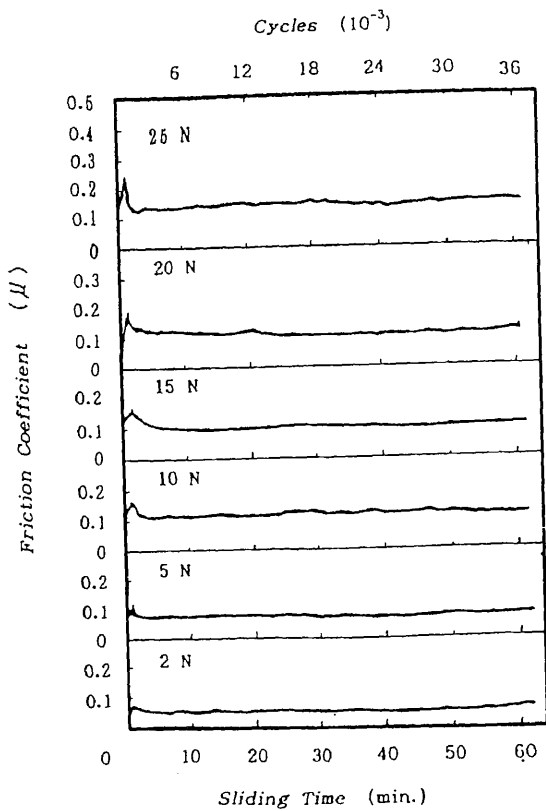


Figure 22. The friction coefficient (μ) vs the wear load measured under the experimental condition shown in table 5.

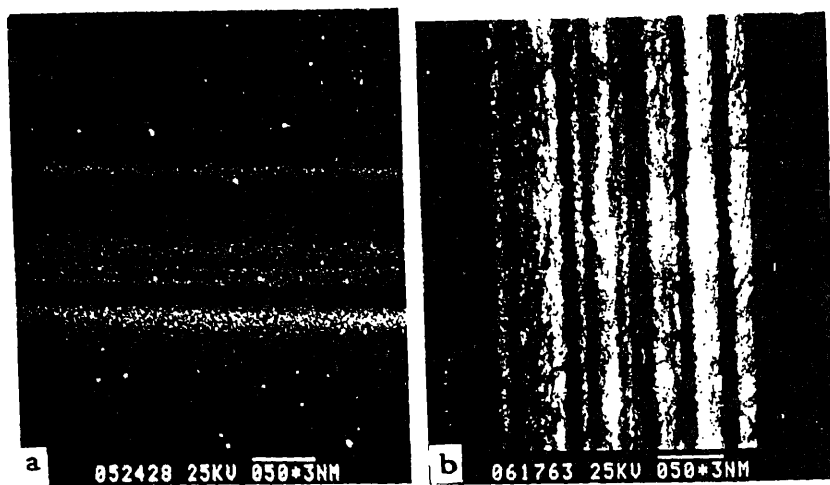


Figure 23. SEM micrographs of wear track produced by a steel ball sliding under a wear load of (a) 5 N, 70 min; (b) 25 N, 35 min at 28% RH.

Table 5. The wear properties of DLC films under different loads*.

Load (N)	2	5	10	15	20	25	5 uncoated
Sliding distances (m)	190	123	165.3	128.5	111.5	80	24
Groove wear volume ($\times 10^6 \text{ mm}^3$)	34.4	124.9	524.3	504.3	308.5	203.92	8781.2
Wear coeff. ($K \times 10^6$)	1.99	4.47	6.99	5.76	3.04	2.24	658.59
AWN	5.7	5.35	5.16	5.24	5.52	5.65	3.18

*All tests were carried out at a temperature of about 27°C and relative humidity of 28%.

The wear properties summarized from the tribological test series are listed in table 5. It can be found that there are two features of the tribological performance of DLC film. The first is that in the wear load range of 2–25 N, the wear coefficients of DLC films are $1.99\text{--}6.99 \times 10^{-6}$, two orders lower than the value for uncoated disc (658.59×10^{-6}). The AWNs also show an average value of 5.44 ± 0.27 , which is much larger than that of uncoated steel disc (about 3.18). Secondly, when the wear loads increase from 2 N to 25 N, the values of AWNs do not vary greatly. These experimental data definitely illustrate that due to dynamic mixing at DLC/Mo/Fe interfaces, DLC films deposited on Mo/steel substrate can notably enhance the tribological performance of AISI 52100 steel, which provides a useful method to apply DLC coatings on steel parts for surface modification under high wear loads.

9. Conclusions

- (i) A narrow energy window between 200 and 400 eV is observed to produce the best results. Raman, XPS, and AES spectra all indicate that DLC films synthesized under 200–400 eV ion bombardment possess valence band structure similar to that of diamond and contain more sp^3 bonds.
- (ii) It is proved that DLC films with very diamond-like properties can be prepared by IBAD process at room temperature. With low-energy-assisted bombardment, DLC films can obtain a high hardness and reach 5100 kgf/mm^2 when bombarded under 200 eV CH^n+ .
- (iii) For practical purposes, DLC on 52100 was chosen for investigation. The tribological studies of DLC/52100 system have yielded very promising antiwear properties. These may allow important applications.
- (iv) The interface between DLC and 52100 can be tailored by high-energy atomic mixing and also by sputtering an intermediate layer such as Mo. Improvement of interface adhesion will greatly help improve the tribological behaviour of DLC on 52100 steel.

Acknowledgements

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Processing and properties of zirconia-toughened alumina ceramics

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Abstract. $\text{Al}_2\text{O}_3\text{:ZrO}_2$ ceramics have been prepared from physically mixed pure oxide powders. The results indicate that careful processing of the starting powders and a two-stage sintering process can avoid expensive processing methods like hot pressing/hot isostatic pressing used for achieving high densification. The mechanical properties were measured and the resultant microstructure studied to explain the toughening behaviour of this material.

Keywords. Al_2O_3 ; ZrO_2 ; toughening; gas over pressure sintering.

1. Introduction

Alumina has been used more frequently than any other type of ceramic in structural applications. A lot of attention has also been given to improving the mechanical properties of this engineering ceramic. For improvement in the mechanical properties, toughness is one of the most important parameters. One way to improve the fracture toughness is the use of the phenomenon of transformation toughening, which is associated with ZrO_2 -containing ceramics.

The concept of toughening alumina ceramics by dispersing zirconia particles in the matrix has been recognized in the last decade. The ceramic containing ZrO_2 can have relatively high value of fracture toughness. This has been attributed to a number of different mechanisms such as stress-induced tetragonal-monoclinic martensitic transformation (Lange 1982; Ruhle *et al* 1986), microcracking due to the stress set up in the matrix around ZrO_2 particles which have undergone martensitic transformation (Claussen *et al* 1982; Ruhle *et al* 1986) and crack deflection around the dispersed ZrO_2 particles.

In the zirconia-toughened alumina, retention of > 10 vol% metastable tetragonal ZrO_2 in the alumina matrix is the key to obtaining the increased room-temperature fracture toughness. However, to retain the metastable tetragonal ZrO_2 it is essential that ZrO_2 grain size be less than some critical size which is reported to be in the range of 0.5 to $0.8 \mu\text{m}$ (Lange and Green 1981; Green 1982; Heuer 1982; Lange 1982; Garvie 1984). Above this critical size, the ZrO_2 grains transform to the monoclinic form.

The high temperatures which are required for the densifications usually result in significant grain coarsening and growth of ZrO_2 particles above the critical size and therefore it is difficult to retain the desired zirconia volume concentration and phase form. Zirconia grain growth occurs at the elevated sintering temperatures of $> 1600^\circ\text{C}$. To meet these requirements, numerous processing approaches have been investigated to achieve lower densification temperature and homogeneous distribution of ZrO_2 in the alumina matrix. The methods which are commonly used include attrition milling, colloidal processing, chemical vapour co-deposited alumina zirconia powders

with a surfactant, co-pyrolysed solutions, hydrothermal reaction of aluminium-zirconium alloys, hydrolysis of zirconium alkoxide in the presence of Al_2O_3 particles, polymer/powder flocculation and sol-gel processing. Leriche *et al* (1988) obtained 99.3% density after attrition milling for 6 h of a mix of two separate slips (of dispersed alumina and zirconia powders) showing same rheological behaviour and sintering in air at 1550°C for 2 h. They could get 100% density for the same samples after hot pressing at 1500°C for 15 min at 30 MPa. Mechanical property measurements were done on their samples by Orange *et al* (1988). For material containing 15 vol% ZrO_2 they obtained a fracture toughness (K_{IC}) value of $6 \text{ MPa m}^{1/2}$. For the hot-pressed sample of the same composition K_{IC} value was around $6\text{--}7 \text{ MPa m}^{1/2}$. Aksay *et al* (1983) started with colloidal suspension which was further milled for 16 h. Using filtration as a consolidation method and sintering at 1600°C in air for 2 h they obtained density $>98.5\%$. White *et al* (1988) started with $0.25 \mu\text{m}$ narrow-sized powders; suspension processing and sintering at 1500°C for 2 h led to a densification around 91–93%.

To avoid grain growth which occurs during pressureless sintering expensive processing like hot pressing/hot isostatic pressing (HIP) is required. However, it is highly desirable to produce structural ceramics with good mechanical properties by conventional processing technique, i.e. normal shaping and simple firing process without expensive processing techniques like hot pressing/hot isostatic pressing. This is particularly advantageous when complicated shapes are required to be made.

The objective of this study was to combine the effects of processing to achieve the high level of densification and fine zirconia phase retention to form toughened alumina-zirconia composites without using expensive high-temperature processing such as hot isostatic or hot pressing.

2. Experimental

The starting powder of $\text{Al}_2\text{O}_3\text{:ZrO}_2$ was made by mixing Alcoa Al6SG alumina with average particle size of $0.52 \mu\text{m}$ (Alcoa, Alumina Company of America, Pittsburgh) and Cerac ZrO_2 (monoclinic, -325 mesh) L-1041 (Cerac, Inc., Milwaukee) to get 15 vol% ZrO_2 in the mix. The mixture was rolled with ZrO_2 grinding media and isopropyl alcohol for 80 h. The slurry was dried under an IR lamp and the powder was sieved through the 100 mesh screen. The particle size of the ZrO_2 in the powder was examined under a JEOL JSM-820 scanning electron microscope (JEOL USA, Inc., Peabody, MA). The zirconia particle size distribution is shown in figure 1. From this figure it is clear that majority of the ZrO_2 particles are in the size range around $0.2 \mu\text{m}$.

The powder was cold isostatically pressed into cylindrical pellets at a pressure of 276 MPa. The samples were sintered in normal air atmosphere at 1450°C for 90 min (heating and cooling rates of 200°C/h). The densities of the samples were measured by Archimedes method. The density was 4.150 g cm^{-3} , which is $\sim 98\%$ of the theoretical density (TD, 4.235 g cm^{-3}).

To enhance further densification, the samples were heat-treated in a graphite furnace. The samples were embedded in boron nitride powder and wrapped in molybdenum foils. The samples were then heated to 1450°C and 10.35 MPa argon gas over pressure was maintained for 2 h.

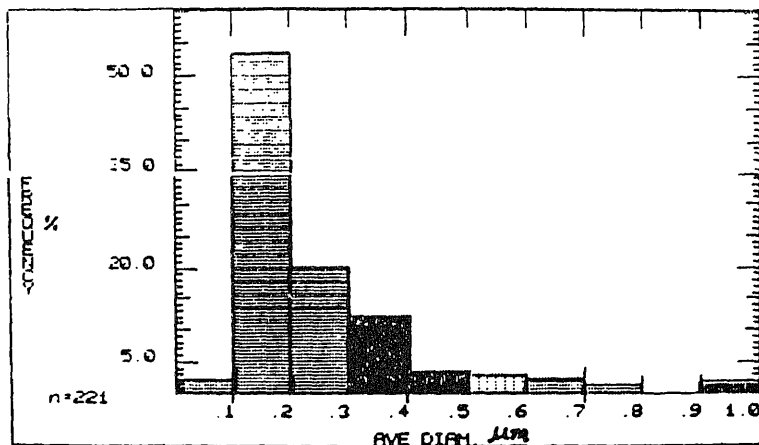


Figure 1. Zirconia particle sizing on the milled $\text{Al}_2\text{O}_3\text{:ZrO}_2$ powder.

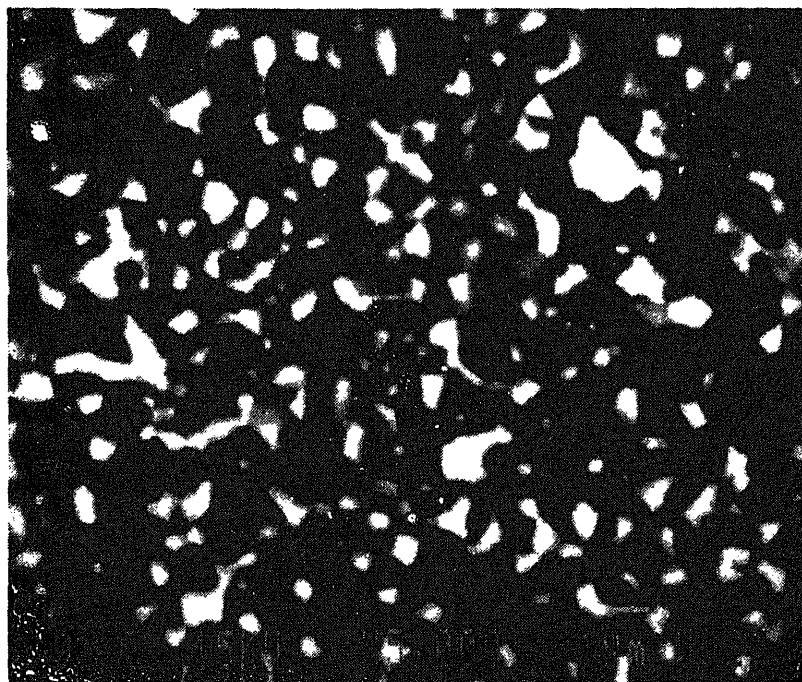


Figure 2. Polished section of sintered $\text{Al}_2\text{O}_3\text{:ZrO}_2$ (BEI).

The densities of the sintered samples were measured after the gas over pressure sintering. Specimens were cut from the sintered samples and the surfaces were polished to a $0.25\text{ }\mu\text{m}$ finish with diamond paste. The samples were chemically etched in 40% hydrofluoric acid (HF) for 2 min to reveal the microstructure. The polished and etched surface as examined under the scanning electron microscope is shown in figure 2. Zirconia particle sizing was done on the polished section and is shown in figure 3.

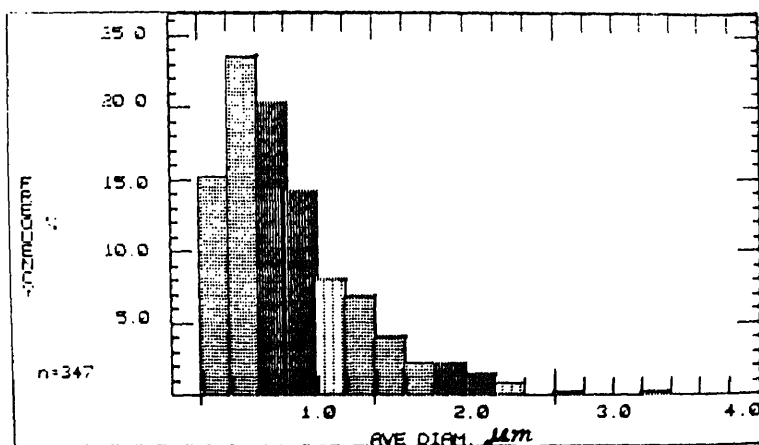


Figure 3. Zirconia particle size distribution on sintered and polished $\text{Al}_2\text{O}_3\text{:ZrO}_2$ surface.

The hardness, fracture toughness and elastic modulus of the polished samples were determined by indentation techniques (Anstis *et al* 1981; Marshall *et al* 1982). To produce well-developed microcracks ($c > 2a$), loads of 10–50 kg were applied depending upon the samples. Controlled flaws were introduced by Vickers diamond pyramid indenter with loads varying between 10 and 50 kg. The specimens were indented at a constant crosshead speed to the selected load and then slowly unloaded. Hardness values were obtained from these measurements. To calculate the toughness of the material it is essential to know its elastic modulus which has been calculated from the Knoop indentation on the sample. This technique of measuring hardness to modulus ratio is based on measurement of the elastic recovery in surface dimensions of Knoop indentation.

3. Results and discussion

The density measurements on the samples after the gas over pressure sintering show that the density was 4.233 g/cm^{-3} . This indicates that the samples were sintered to near theoretical density (99.95% of TD). This also confirms that the samples were sintered to closed porosity state by normal air sintering and the gas over pressure sintering was helpful in eliminating the pores further to get full densification. Thus by careful processing of the starting powder (i.e. by making sure that ZrO_2 particles are fine and majority of them are within narrow size range) and a combination of air sintering and gas over pressure sintering, it should be possible to densify even complicated shapes of this material without the necessity of expensive processing methods.

The room-temperature hardness and fracture toughness values for this material (values reported here are the average of several measurements) are as follows: Hardness (GPa) 17.8, E/H 23.6, and fracture toughness ($\text{MPa m}^{1/2}$) 4.8.

The data can be explained in the light of the observed microstructure. Fine zirconia particles are retained after sintering as seen in figure 2. This is further clear from the zirconia particle size distribution on the sintered sample as shown in figure 3. These

fine zirconia particles are possibly in the tetragonal form. Presence of these fine zirconia particles gives rise to transformation toughening effects in the wake of the advancing crack and this must be the main contributing factor for the observed hardness and fracture toughness of this material.

Conclusions

It has been demonstrated that high-density zirconia-toughened alumina ceramics with good mechanical properties can be obtained by careful processing of the initial powder and a combination of air sintering and gas over pressure sintering. These results also indicate that material can be densified to high density without the necessity of expensive hot pressing/hot isostatic pressing.

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Microwave sintering of yttria-containing tetragonal zirconia polycrystal (Y-TZP) ceramics

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Abstract. Sintering of yttria-containing tetragonal zirconia polycrystal (Y-TZP) ceramics was performed in a single-mode cylindrical cavity applicator CMPR-250 operating at 2.45 GHz in the TM_{012} mode. High heating rates at low power levels were achieved. Rapid heating and cooling resulted in a fine-grain microstructure.

High-purity submicron Y-TZP powders were sintered from an initial green density of 60% to final sintered density close to the theoretical density. Microwave sintering offers potential for improving microstructural properties through controlled development of uniform microstructure.

Keywords. Microwave sintering; Y-TZP; single-mode applicator.

Introduction

Tetragonal zirconia polycrystal (TZP) ceramics are one of the most promising materials because of their excellent thermal and mechanical properties. Yttria-stabilized tetragonal zirconia (Y-TZP) ceramics consist of tetragonal zirconia (ZrO_2) grains containing around 2–3 mol% Y_2O_3 in solid solution. These ceramics are useful as adiabatic engine components in the form of ceramic–metal composite system for thermal insulation. Their low thermal conductivity and high thermal expansion reduce the difficulties encountered with ceramic–metal attachment. The ionic conductivity of TZP ceramics is ionic, which remains reasonably constant over several cycles and for reasonable length of time (Yamamoto *et al* 1990) and hence they are attractive as an electrolyte for solid oxide fuel cell applications in the temperature range 900–1000°C. They have also impressive mechanical properties and hence are used as structural material. All these applications require high level of densification in a sintered body.

The toughness of these materials is due to the tetragonal-to-monoclinic transformation which occurs in the process zone around the advancing crack front (Porter *et al* 1979). Stabilization of zirconia in the tetragonal phase is, therefore, critical. However, to retain the metastable tetragonal ZrO_2 , it is essential that ZrO_2 grain size be less than some critical size which is reported to be in the range of 0.5 to 0.8 μm (Rangan and Green 1981; Green 1982; Garvie 1984). Above this critical size, the ZrO_2 grains transform to the monoclinic form.

The high temperatures which are required for the densification during conventional sintering processes usually result in significant grain coarsening and growth of ZrO_2 particles above the critical size. Therefore, it is difficult to retain the desired zirconia tetragonal phase form. To meet these requirements, numerous processing approaches have been investigated to achieve lower densification temperature.

interest as the realization of the technique's utility has increased. Microwave heating is fundamentally different from conventional heating processes as heat is generated within the material. Microwave energy is deposited instantaneously and volumetrically within the bulk of the ceramic. Thermal gradients and heat flow are in reverse direction in comparison to conventional heating. This, coupled with high heating rate, allows uniform pore elimination and ultrafine microstructure. An excellent review on ceramic processing by microwaves is given by Sutton (1989).

Good uniformity in microwave sintering requires a knowledge of the high-temperature microwave properties of the material as well as the ability to modify and control them.

The difficulties encountered in efficient microwave sintering of ceramics can be reduced by using a resonant cavity. Single-mode resonant systems can be designed to yield very high electric field strength which, in turn, results in high heating rates. The field inside the cavity can be considerably larger than the field outside. This is due to an increase in the quality factor of the cavity (Asmussen *et al* 1987). Power absorbed by the material being proportional to its dielectric loss factor and the square of the electric field strength (Chabinsky and Eves 1986; Tinga 1986), the use of single-mode applicator definitely helps in putting more power even in materials with low dielectric loss.

Practical-size samples of Al_2O_3 and $\text{Al}_2\text{O}_3\text{:ZrO}_2$ were successfully sintered by using single-mode applicator and the results are published in detail elsewhere (Patil *et al* 1991a, b).

The objective of this study was to show the feasibility of using a single-mode applicator for microwave sintering of the Y-TZP ceramics.

2. Experimental set-up

The experimental system consists of a variable-power CW microwave power supply (3 kW operating at 2.45 GHz), two circulators and matched dummy loads, WR-284 wave guide network, forward and reflected power meters (which measure the incident power P_i and the reflected power P_r), a coaxial input coupling system, Accufibre temperature measurement system (Model 100 C, Accufibre, Inc., Beaverton, OR) and Wavemat cavity CMPR-250 (Wavemat Inc., Plymouth, MI). This particular cavity has the ability to focus and match the incident microwave energy into the process material. It can be internally tuned. The details are given elsewhere (Patil *et al* 1991a).

3. Sample preparation and experiment

We have used two types of powders for this study. The first powder TZP-O was as received from Ferro (NZP-A3Y, ARP 5863; Ferro Corporation, Cleveland, OH). The vendor's data show that the average zirconia grain size is $0.274\ \mu\text{m}$ and yttria content 3 mol%. The other powder TZP-CHEM was made by a chemical route. The preparation procedure is as follows. Aqueous solutions of appropriate amounts of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Johnson Matthey, Alfa Products, Ward Hill, MA) were mixed to get the desired composition with Y_2O_3 as 2.5 mol%. After homogeneous mixing, water was evaporated slowly and thoroughly. The dried mix was calcined at 1100°C

for 2 h at a heating/cooling rate of $6^{\circ}\text{C}/\text{min}$. The calcined powder was washed with deionized water to make it free of Cl^- radicals. The washed powder was dried under an infrared lamp. The washed and dried powder was milled with isopropyl alcohol using zirconia media for 50 h. The slurry was dried under an infrared lamp and the dried powder was sieved through a 100 mesh screen. The average zirconia grain size as seen under the JEOL JSM-820 scanning electron microscope (JEOL USA, Inc., Woburn, MA) was around $0.3\text{ }\mu\text{m}$.

These powders were isostatically cold-pressed into cylindrical pellets of approximate size $25.4\text{ mm dia.} \times 25.4\text{ mm height}$ at a pressure of 276 MPa. The pellets were kept at 100°C in an oven for 12 h to remove moisture. The green densities of the pellets were around 60% of the theoretical density.

The pellet was embedded in alumina fibre insulation. The insulated pellet was kept at the centre of the base plate of the cavity on a boron nitride platform. The incident microwave power was coupled with the help of the coupling probe. A hole of approximately 3 mm was drilled through the insulation to view the sample surface by the Accufibre optical pyrometer system through a non-radiating opening on the wall of the cavity. The samples were processed in the cavity according to the heating schedule shown in figure 1. The temperature shown here is the surface temperature of the sample. It was essential to control the heating and cooling rates to get crack-free samples. The total microwave power (forward and reflected power together) did not exceed 1 kW. The densities of the samples were measured by Archimedes principle. The fractured surfaces of the samples were seen under SEM.

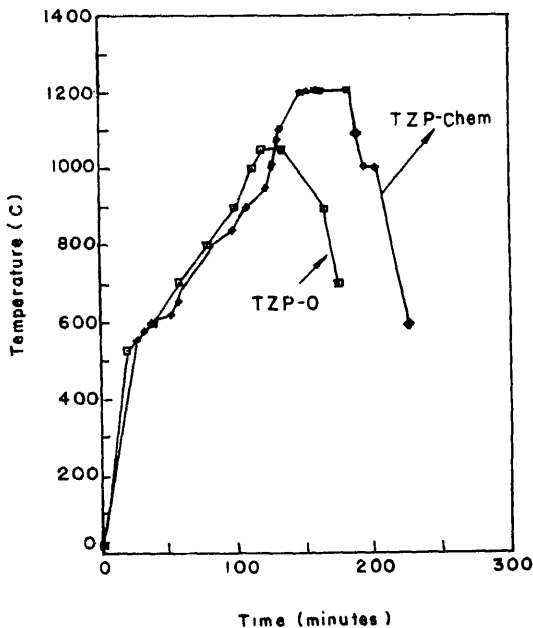


Figure 1. Microwave sintering schedule for TZP samples.

4. Results and discussion

The density measurement on the samples show that the sample TZP-O was sintered to 96.85% of the theoretical density in 3.16 h (this includes heating, cooling and hold time at high temperature) and the sample TZP-CHEM was sintered to theoretical density in 4 h.

The sintering consisted of two steps: preheating and sintering stage. The sample was initially heated for a few min at a constant low power. Attempts to reach the final sintering temperature without preheating, i.e. by raising the input power, gave rise to hot spot formation, arcing and eventual cracking of the samples. To achieve sintering uniformity it was necessary to insulate the sample. The gradual increase in power is also essential to get proper densification. With careful control of these conditions thermal runaway which is generally observed in the microwave sintering experiments has been avoided. The densification of the sample was noted by an increase in the reflected power, as the sample fails to absorb more power after densification and hence the reflected power increases. Controlled cooling was essential to avoid cracking of the sample due to thermal shock.

The microstructures/fractured surfaces of the samples as seen under SEM are shown in figures 2 and 3. Fine and uniform microstructure is seen. Microwave sintering should help in retaining zirconia in the metastable tetragonal phase because the sample passes more rapidly through the lower-temperature regime where surface diffusion is relatively more important and the fine-grain microstructure is raised to high temperature where grain boundary and lattice diffusion dominate over surface

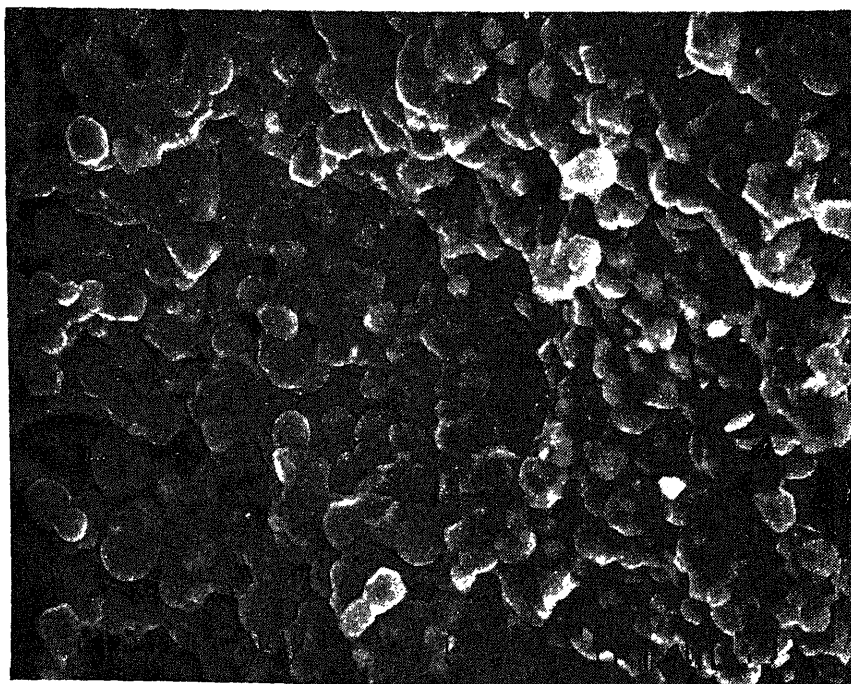


Figure 2. Fractured surface of sintered TZP-O.

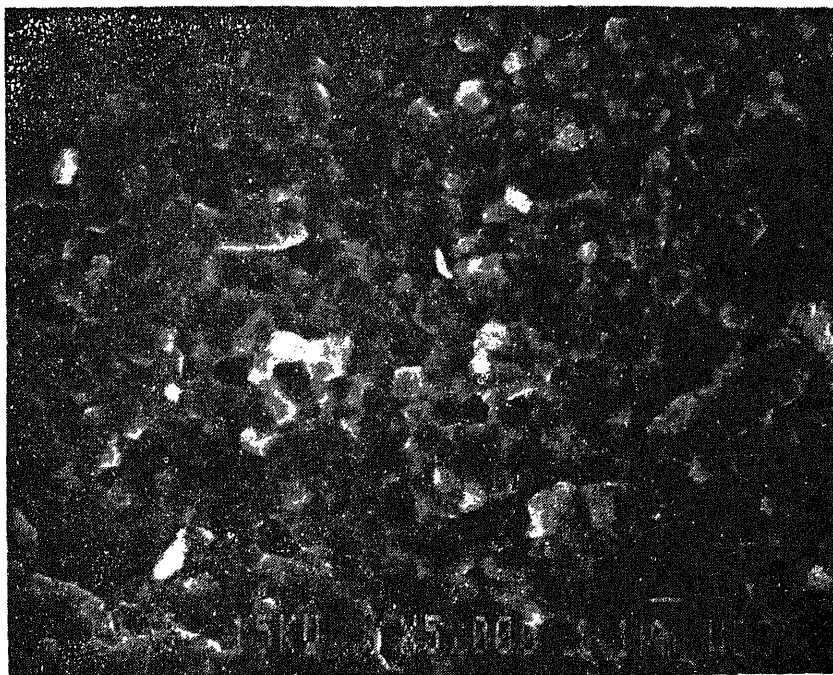


Figure 3. Fractured surface of sintered TZP-CHEM.

diffusion. Although the powder TZP-O was fine it contains 2% organic binder. Since our microwave sintering schedule was faster, it is likely that the organic binder was not removed at the preheating stage and it might have decomposed and evaporated at the rapid sintering stage, hindering complete pore elimination.

6. Conclusions

Y-TZP ceramic samples of different types were successfully densified from initial green density of ~60% to densities close to the theoretical density by using a single-mode applicator operating in the TM_{012} mode at 2.45 GHz. Practical-sized samples of this material have been truly microwave-sintered without use of any binder or susceptor.

Fine and uniform microstructure in Y-TZP ceramic can be achieved by rapid sintering in a microwave cavity.

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Structural characterization of gel-grown neodymium copper oxalate single crystals

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Abstract. Sparingly soluble neodymium copper oxalate (NCO) single crystals were grown by gel method, by the diffusion of a mixture of neodymium nitrate and cupric nitrate into the set gel containing oxalic acid. Tabular crystal, revealing well-defined dissolution figures has been recorded. X-ray diffraction studies of the powdered sample reveal that NCO is crystalline. Infrared absorption spectrum confirmed the formation of oxalato complex with water of crystallization, while energy dispersive X-ray analysis established the presence of neodymium dominant over copper in the sample. X-ray photoelectron spectroscopic studies established the presence of Nd and Cu in oxide states besides $(C_2O_4)^{2-}$ oxalate group. The intensities of Nd ($3d_{5/2}$) and Cu ($2p_{3/2}$) peaks measured in terms of maximum photoelectron count rates also revealed the presence of Nd in predominance. The inductively coupled plasma analysis supports the EDAX and XPS data by the estimation of neodymium percentage by weight to that of copper present in the NCO sample. On the basis of these findings, an empirical structure for NCO has been proposed. The implications are discussed.

Keywords. Neodymium copper oxalate; gel growth; characterization; XRD; IR; EDAX; XPS.

Introduction

The growth of sparingly soluble inorganic crystals employing gel technique (Henisch 1970) is well established and extensive work has been reported in the literature on the morphologies (Raju 1983a, b, c, 1986), nature of dislocations (Raju 1985), as well as on the mechanical behaviour (Raju *et al* 1984) in the case of gel-grown calcium phosphate dihydrate single crystals. It is well known that the rare-earth compounds inhibit high-temperature superconductivity and oxalate crystals show good ionic conductivity (George Verghese *et al* 1990), hence it is interesting to study the characteristics of rare-earth mixed oxalates. Caillaud *et al* (1988) have shown that superconducting compounds can be obtained by the controlled precipitation of oxalates followed by calcination. Further, researchers have proved that oxides like lanthanum copper oxide exhibit superconductivity up to 40 K (Beille *et al* 1987).

We report here the work carried out on the gel-grown mixed oxalate crystals of copper and neodymium (neodymium copper oxalate, NCO) and their characterization employing X-ray diffraction (XRD), IR, energy dispersive X-ray analysis (EDAX), X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma (ICP)

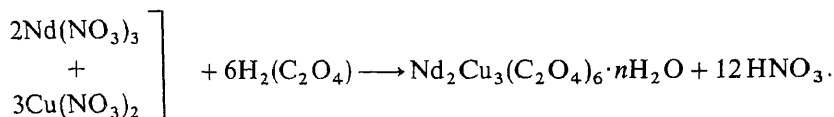
studies, which throw light on the kinetics of chemical reactions, the qualitative and quantitative analyses of heavy elements present in the mixed oxalates, besides the presence of their chemical states.

These results help in speculating on the empirical structure of NCO sample.

2. Experimental observations and results

2.1 Growth of NCO in gels

Acidified silica gel of specific gravity 1.03 g cm^{-3} was used as the reacting medium. A mixed solution of neodymium nitrate and cupric nitrate with nitric acid was used as the outer reactant above the gel at room temperature. The outer reactant diffused into the set gel containing oxalic acid. The following reaction takes place, producing bluish pink colloidal precipitate of mixed oxalates of neodymium and copper ($\text{Nd}_2\text{Cu}_3(\text{C}_2\text{O}_4)_6 \cdot n\text{H}_2\text{O}$) and nitric acid:



The nitric acid present in the gel medium may induce nucleation from the precipitate resulting in crystallization. A large number of well-defined bluish pink transparent microcrystals were observed just below the interface, while isolated crystals of relatively bigger sizes appeared at greater depths in the gel. The optimum conditions for the growth of good single crystals were found to be pH 5 of the gel and 0.5 molarity of each of the nitrates in 1:1 by volume in the outer reactant.

The proposed empirical structure of neodymium copper oxalate is given in figure 1.

Figure 2 shows an SEM of the basal plane of an NCO crystal (of size $5 \times 3 \times 0.5 \text{ mm}^3$) grown at greater depth in the gel. The basal plane can be seen to have relatively curved edges and corners. Careful examination of microstructures on the basal plane reveals crystallographically oriented dissolution figures (figure 3) suggesting thereby the single-crystalline nature of the NCO sample.

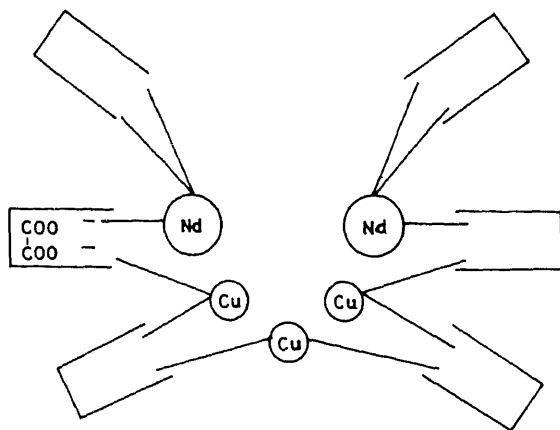


Figure 1. Proposed empirical structure of NCO.



Figure 2. SEM picture of gel grown NCO.

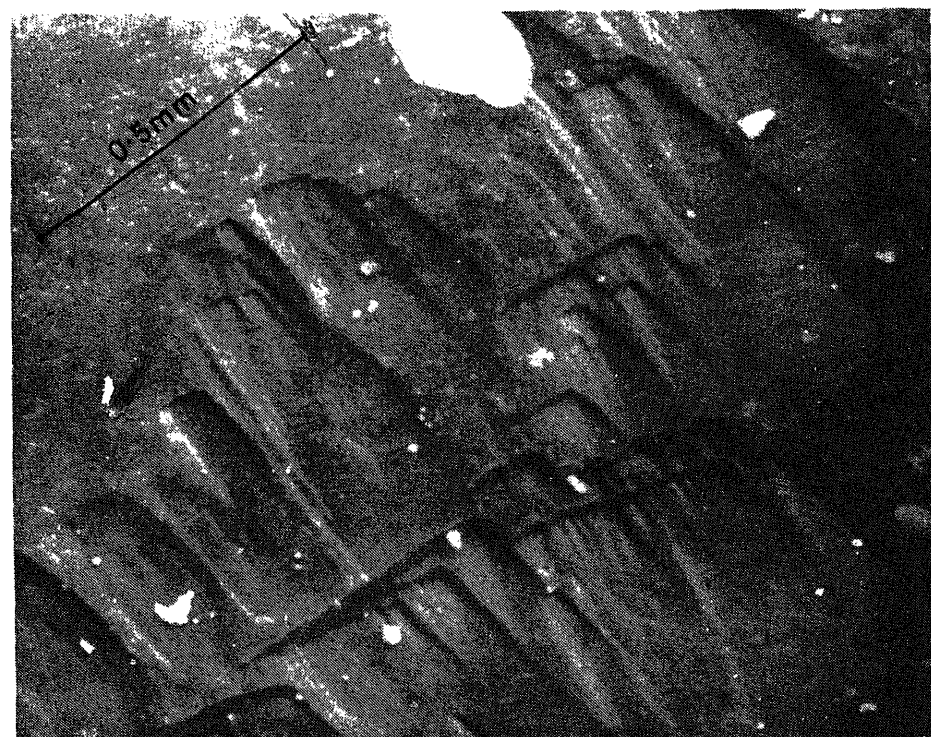


Figure 3. SEM picture showing dissolution figures on basal plane of NCO.

2.2 Characterization of NCO

2.2a XRD studies: In order to confirm the crystallinity, the powder X-ray diffraction pattern of NCO sample (figure 4) was taken in a Philips XRD PW 1050/70 with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). The revelation of well-defined Bragg peaks at specific (2θ) angles suggests that NCO is ordered, meaning crystalline nature of the sample. It is worth mentioning here that the d values of the Bragg peaks in the XRD pattern of powdered NCO (figure 4) match quite well with the d values of the Bragg peaks relating to the XRD pattern recorded for powdered neodymium oxalate dodecahydrate.

2.2b IR absorption studies: The IR absorption spectrum of NCO sample (figure 5) in KBr matrix was recorded in a Perkin Elmer model 530.

The sample has water of crystallization as evidenced by the broad peak at $3000\text{--}3800 \text{ cm}^{-1}$ (relating to antisymmetric and symmetric OH stretchings) and at 1630 cm^{-1} (relating to HOH bending).

That the NCO sample has oxalate (C_2O_4) $^{2-}$ ions is supported by the revelation of well-pronounced peaks at 1720 cm^{-1} [$\gamma_a(\text{C}=\text{O})$], 815 cm^{-1} [$\delta(\text{O}-\text{C}=\text{O}) + \gamma(\text{MO})$], 610 cm^{-1} , 500 cm^{-1} [ring deformation + $\delta(\text{O}-\text{C}=\text{O})$], 390 cm^{-1} [$\delta(\text{O}-\text{C}=\text{O}) + \gamma(\text{CC})$] (perhaps crystal water) and $335 \text{ cm}^{-1}(\pi)$.

2.2c Energy dispersive X-ray analysis (EDAX): In order to establish the elemental incorporation (like Nd and Cu) in the NCO crystals, EDAX was done. The integrated counts of X-ray photoelectrons relating to the elemental peaks taken for a definite time interval have been helpful in getting the approximate quantitative content of their respective elements reported in the present investigation.

•The tiny crystals of NCO were mounted on to an aluminium stub, the surfaces of which were coated with a thin layer of gold to make them electrically conducting. The surfaces were examined in the EDAX analyser No. 711, an accessory to the Philips SEM model 501. The EDAX picture of NCO so recorded is shown in figure 6.

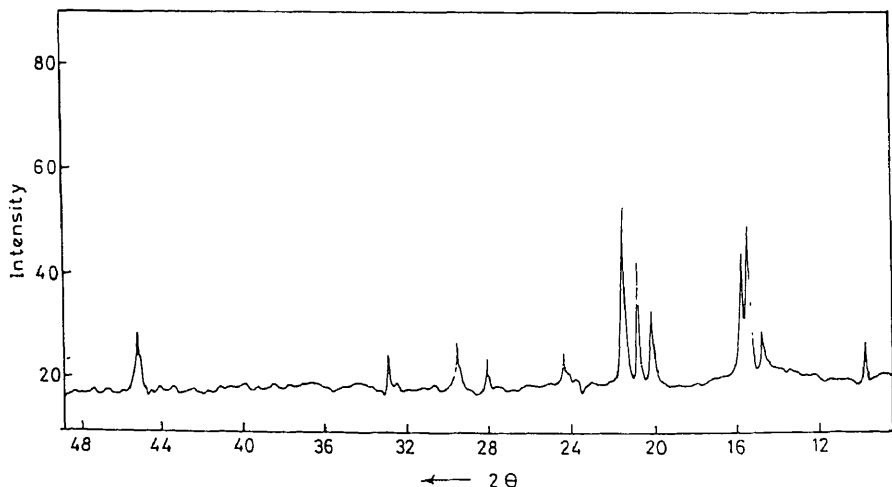


Figure 4. Powder XRD pattern of NCO.

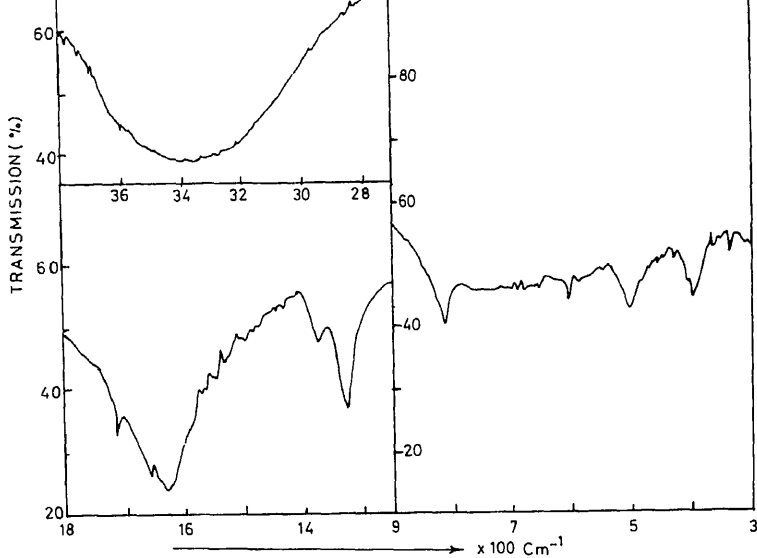


Figure 5. IR absorption spectrum of NCO.

79 8040EV K Z29 CU
VS: 2500 HS: 20 EV/CH

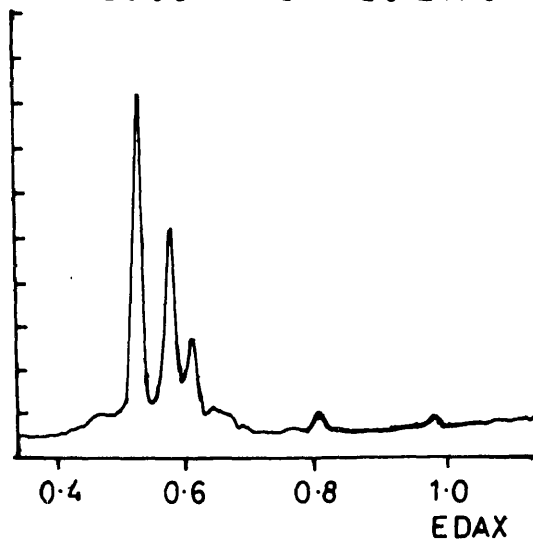


Figure 6. EDAX pattern of NCO.

The three dominant peaks positioned at 5.23, 5.72 and 6.088 keV (in the left hand side of figure 6) correspond quite well to the L_{α} , L_{β} and L_{γ} energies of neodymium, while a small hump at 8.04 keV corresponds to K_{α} line of copper (reported in the EDAX international chart), thereby establishing the presence of heavy elements (like

Nd and K_{α} of copper gives a strong clue that neodymium is dominant over copper in the sample.

The integrated count of X-ray photoelectrons relating to neodymium (L_{α}) collected for 150 sec was found to be 60,094 while for copper (K_{α}) the integrated count was 6144.

A very small hump for copper K_{α} at 8.04 keV compared to neodymium L_{α} at 5.23 keV observed in figure 6 is supported by the smaller integrated count of X-ray photoelectrons for copper K_{α} relative to neodymium L_{α} .

2.2d *XPS studies:* In order to further establish the constituents incorporated in NCO sample besides their chemical states, XPS studies are undertaken.

For the sample preparation, NCO is nicely powdered and a pellet of 1 cm diameter and 1 mm thickness was formed using a hydraulic press by applying a pressure of 1.1 tons per cm^2 . XPS spectra were taken in VG scientific ESCALAB MK II, by irradiating the sample with monochromatic soft X-rays (Mg K_{α} ; photon energy 1253.6 eV). The constant analyser energy was 50 eV and the resolution of the system was about 0.7 eV.

Figure 7 shows the XPS peak relating to Nd $3d_{5/2}$ with the binding energy centred at 980 eV, with the maximum count rate (MCR) of photoelectrons 8958, while figure 8 relates to the XPS peak of Cu $2p_{3/2}$ having binding energy around 933.6 eV (MCR 215).

It is well known that the count rates of photoelectrons relating to an XPS peak,

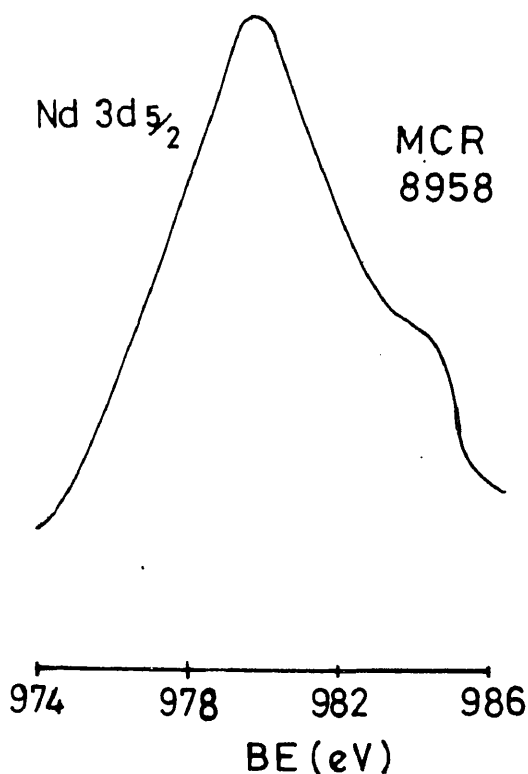


Figure 7. XPS peak of Nd ($3d_{5/2}$) of NCO.

meaning thereby intensity, is a measure of the quantity of the concerned element present in the material (Riggs and Parker 1975). The XPS observation regarding the MCRs of Nd and Cu supports the EDAX observation that Nd is more dominant than copper in the NCO sample.

The binding energy values relating to Nd ($3d_{5/2}$) and Cu ($3p_{3/2}$) in figures 7 and 8 agree quite well with the literature values (Wagner *et al* 1978) corresponding to their oxide states (Nd_2O_3 and CuO in the present case).

Figure 9 is the XPS region of carbon 1s of NCO sample in which it is clear that there are two peaks at binding energy values 287 and 290 eV. The first peak at 287 eV is attributed to the adventitious hydrocarbon being contributed from the laboratory environment or from the glove box, while the latter peak at the higher binding energy (290 eV) relates to the oxalate (C_2O_4) $^{2-}$ group. This shift towards the higher binding energy corresponding to the oxalate group with respect to the first peak (287 eV) is due to the higher electronegativity of (C_2O_4) $^{2-}$.

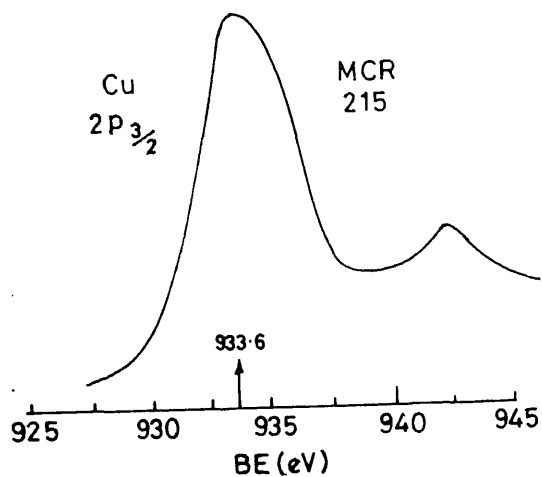


Figure 8. XPS peak of Cu ($2p_{3/2}$) of NCO.

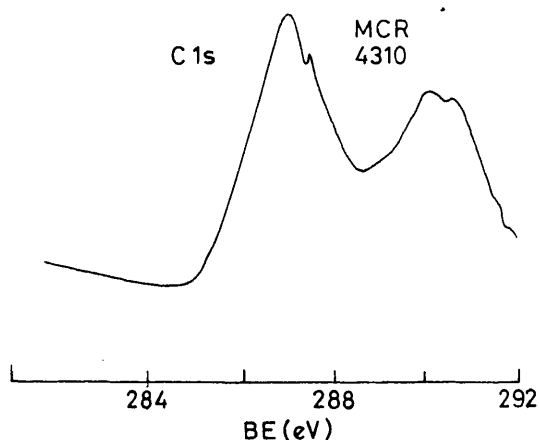


Figure 9. XPS peak of C 1s of NCO.

Thus XPS, though a method for surface analysis, is a powerful technique in identifying not only the constituents present in the sample but also their respective chemical states.

2.2e Inductively coupled plasma (ICP) analysis: The atomic emission spectrum of NCO by inductively coupled argon plasma was studied. Fifty to 55 mg of NCO was dissolved in HCl and the solution made up to 25 ml. The quantitative analysis of neodymium and copper was carried out with the calibration standards of Nd_2O_3 and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in the range 0, 10, 20, 50 and 100 ppm. The concentrations of neodymium and copper (in ppm) were found to be 1170 and 6 ppm respectively. These computations are in very good agreement with the findings of EDAX and XPS confirming the dominance of neodymium over copper in NCO sample.

3. Discussion

The observation that NCO grown by gel is crystalline in nature is obviously evident by the revelation of tabular crystal at the greater depths in the gel, having geometrical edges and corners. On careful examination of the basal plane of the crystal, a large density of crystallographically oriented dissolution figures was observed. After the cessation of growth, during harvesting of the crystals, the acidic resultant (HNO_3) in the gel might have sparingly dissolved the sharp edges and corners thereby rounding them (figure 2) and also the basal plane producing crystallographically oriented dissolution figures (figure 3). The crystallinity of the NCO sample was further ascertained by powder XRD (figure 4) which revealed well-defined Bragg peaks whose d values match well with the d values of Bragg peaks relating to powdered neodymium oxalate, which is reported as crystalline (Weast and Lide 1990). The IR absorption spectrum of NCO (figure 5) establishes the presence of oxalato complexes in the sample besides its crystallinity as evidenced by the broad peak ($3000\text{--}3800\text{ cm}^{-1}$) relating to the water of crystallization, agreeing quite well with the reported values in the literature (Nakamoto 1978). A small hump at 8.04 keV (K_α peak of copper) in EDAX of NCO sample (figure 6) relative to the predominant peak L_α of Nd is well in agreement with the integrated count of photoelectrons of L_α of neodymium as 60,094 compared to 6144 for K_α of copper, both collected for 150 sec. The XPS results support well that Nd and Cu are in their oxide states (figures 7 and 8) getting linked to O^- of $(\text{C}_2\text{O}_4)^{2-}$, the latter being evidenced by the XPS of C 1s (figure 9). These results are in excellent agreement with the proposed empirical formula for NCO (figure 1). The MCRs of photoelectrons relating to $3d_{5/2}$ peak of neodymium (8958) and $3p_{3/2}$ peak of copper (215) reestablish the EDAX and ICP results that Nd is dominant over copper in NCO sample.

The dominance of Nd over copper is explained as follows.

The rare earth neodymium is a hard acid and oxalate is a hard base and hence has stronger affinity for neodymium oxalate formation. Copper belongs to soft acid and in presence of neodymium has a very weak role in the formation of copper oxalate. This may be the reason for the dominance of neodymium over copper in the NCO sample (Huheey 1983).

5. Conclusion

It is concluded that the gel-grown NCO sample reported in the present work (i) is crystalline in nature as evidenced by the well-defined edges and corners (though curved later) as well as by the revelation of crystallographically oriented dissolution figures (figures 2 and 3), (ii) is ordered and crystalline (XRD), (iii) accounts for the presence of oxalato complex by the revelation of its characteristic peaks and of lattice water by the broad peak at $(3000\text{--}3800\text{ cm}^{-1})$ (IR), (iv) has Nd and Cu established qualitatively and quantitatively (EDAX), (v) has Nd and Cu in their oxide states (XPS) getting linked to O^{2-} of oxalate groups (figure 1), and (vi) has Nd in abundance relative to Cu as evidenced by the integrated counts of their X-ray photoelectrons in EDAX and XPS) and by their quantitative presence estimated by ICP analysis.

Acknowledgements

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Photoluminescence of gold-doped (Zn, Cd)S mixed phosphors

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Abstract. (Zn, Cd)S: Au, Cl mixed phosphors were prepared in nitrogen atmosphere with various concentrations of impurities. Photoluminescence (PL) spectra were obtained. The peak of the PL spectrum shifts towards longer-wavelength values with increasing replacement of zinc by cadmium in the host lattice. The PL efficiency was found to decrease with increasing CdS content whereas lattice constants increased with increasing CdS concentration.

Keywords. Photoluminescence; mixed phosphors; PL spectra; X-ray diffraction; II–VI compounds; optoelectronic materials.

1. Introduction

Recent developments in the field of optoelectronic devices have created requirements for high-purity semiconductor materials like II–VI compounds and their alloys. The need for high-quality materials has led to the development of novel semiconductor growth and processing technologies. Characterization techniques, mainly photoluminescence (PL) spectroscopy (Dean 1973; White 1979), have been considerably improved in sensitivity and versatility over the years. The PL technique provides a contactless, nondestructive means for the analysis of semiconductors. Considerable progress has been made in understanding the photoluminescence phenomenon in ZnS, CdS phosphors activated with copper (Froelich 1952; Piper and Williams 1952; Mater and Cera 1962) and silver (Bube 1953; Mater 1957; Gurvich 1966), but to date the least attention has been paid to the investigation of photoluminescence in gold-doped (Zn, Cd)S mixed phosphors. There is still considerable use for sulphide phosphors in cathode ray tube screens for televisions and electroluminescent devices (Elmanharawy and Abdel Kader 1980; Abdel Kader and Bryant 1986). Therefore characteristics of the gold-activated series are of practical interest. The present paper reports preparation, photoluminescent properties and crystallographic studies of gold-doped (Zn, Cd)S mixed phosphors.

2. Experimental

The gold-doped (Zn, Cd)S mixed phosphors were prepared by firing a mixture of luminescent grade ZnS and CdS (Fluka, Switzerland), auric chloride (AuCl_3) and sodium chloride in appropriate proportions. The activator concentration was varied from 0 to 10,000 ppm and CdS content was varied from 0 to 40 per cent. The charge was placed in a silica crucible. The firing was done in a silica tubular furnace

maintained at 1100°C and 800°C in the inert atmosphere of flowing nitrogen gas. After the firing was complete, the charge was taken out of the furnace and immediately crushed and finely powdered to have a uniform particle size. Although defects are produced during grinding but better repetitive results are obtained in case of ground phosphors as compared to that in unground phosphors.

For photoluminescence studies a 365 nm (UV) filter was placed between the 600 W tungsten-halogen lamp and the phosphor, so that PL excitation may take place at 365 nm and PL emission spectra can be obtained in the visible region. The absorption spectra of (Zn, Cd)S phosphors had a peak around 365 nm. The PL spectra was recorded by placing phosphor adhered on glass plate using toluene near the entrance slit of the grating monochromator. Near the exit slit of the monochromator, an EMI-6199 photomultiplier tube was placed, whose output was connected to a digital picoammeter. The variation of PL intensity with the activator concentration was determined by plotting a curve between the total PL intensity i.e. the area below the PL intensity vs wavelength, and activator concentration.

Crystal structures of the various phosphors were identified and X-ray powder pattern taken by the Philips X-ray diffractometer and an 11.48 cm diameter camera using nickel filtered CuK_α radiation of wavelength 1.54175 Å. All X-ray powder patterns were obtained in terms of the intensity of the diffracted X-ray beam as a function of the diffraction angle 2θ . The interplanar spacings were measured to an accuracy of 0.001 Å near 2θ equal to 64°. The lattice parameters a and c of the unit cell were calculated by the following procedure (Kaelbe 1967).

(a) Indexing pattern of cubic system:

For cubic crystals, lattice spacing is given by

$$d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2}. \quad (1)$$

The values of interplanar distance of the corresponding diffraction peaks were calculated using Bragg's law,

$$2d_{hkl} \sin \theta = \frac{hc}{E_{hkl}} = \lambda. \quad (2)$$

From (1) and (2),

$$\sin^2 \theta / (h^2 + k^2 + l^2) = \frac{\lambda^2}{4a^2} = \text{constant}. \quad (3)$$

The lattice parameter a for cubic crystallites was estimated from (3).

(b) Indexing pattern of hexagonal system:

For hexagonal crystals, lattice spacing is given by

$$\frac{1}{d^2} = (4/3a^2)(h^2 + hk + k^2) + l^2/c^2. \quad (4)$$

Combination of Bragg's law and plane spacing equation for hexagonal yields the relation

$$\sin^2 \theta = A(h^2 + hk + k^2) + cl^2, \quad (5)$$

here

$$A = \lambda^2/3a^2, \quad \text{and} \quad c = \lambda^2/4c^2. \quad (6)$$

or $l = 0$, (5) gives

$$\sin^2 \theta = A(h^2 + hk + k^2), \quad (7)$$

where possible values of $(h^2 + k^2 + l^2)$ are 1, 3, 4, 7, etc. The values of lattice parameters a and c were estimated using (5), (6) and (7).

Results

The PL spectra of gold-doped (Zn,Cd)S mixed phosphors for given activator concentration (1000 ppm) are shown in figure 1. It is observed from the figure that the peak of the PL spectrum shifts towards longer-wavelength side with increasing CdS content.

Figure 2 illustrates the variation of λ_m , the wavelength corresponding to the peak PL intensity, with CdS content for these phosphors. It is found that λ_m varies from 476 nm to 588 nm for CdS variation from 0 to 40 per cent in hexagonal (Zn,Cd)S: Au, Cl mixed phosphors. It is observed from figure 3 that for a given activator concentration (1000 ppm), the PL intensity decreases with increasing CdS content in gold-doped (Zn,Cd)S hexagonal phosphors.

Figure 4 shows the dependence of PL intensity on activator concentration in (Zn,Cd)S: Au, Cl phosphors. It is seen that the PL intensity is maximum for a particular

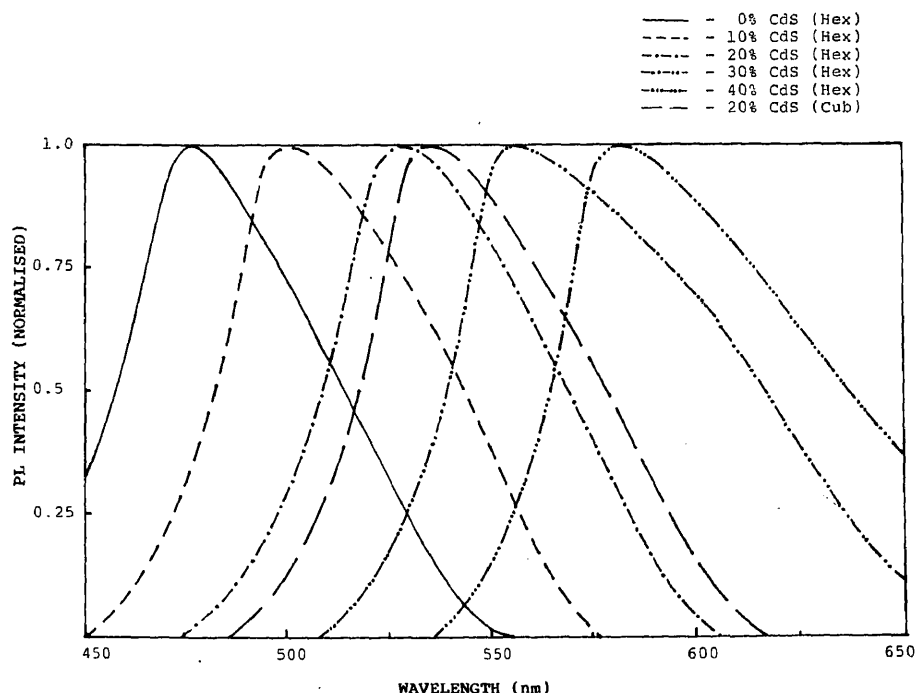


Figure 1. PL spectra of (Zn,Cd)S:Au,Cl mixed phosphors.

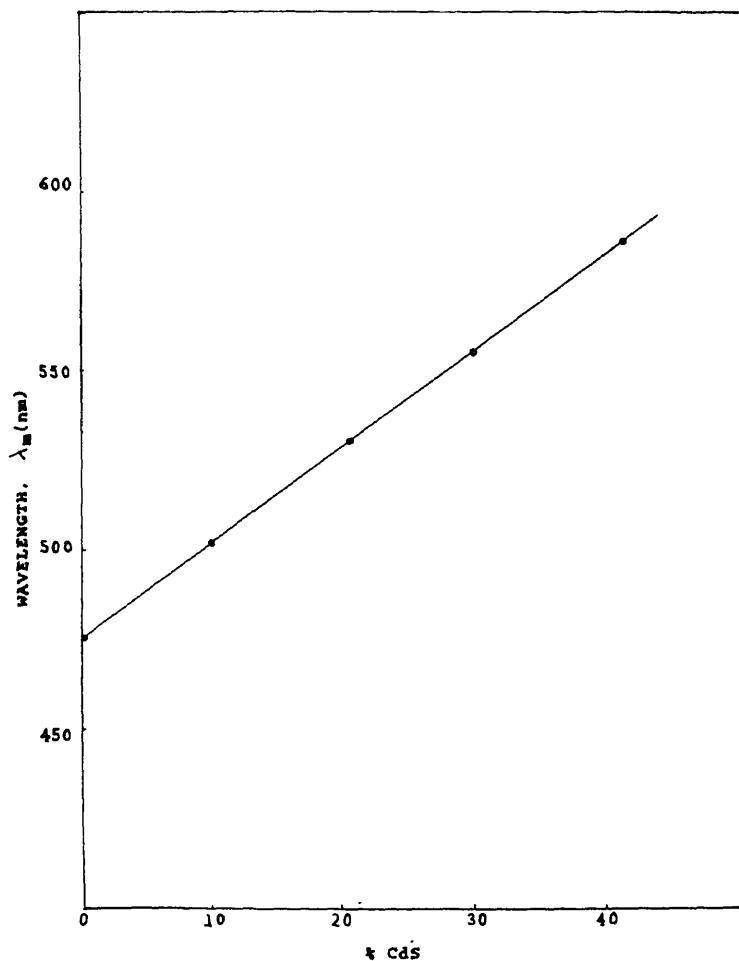


Figure 2. Effect of CdS concentration on wavelength corresponding to peak PL intensity (λ_m) of hexagonal (Zn, Cd)S: Au, Cl phosphors.

activator concentration. Furthermore, the activator concentration for which PL intensity attains maximum value increases with increasing CdS content.

The diffraction patterns for gold-doped (Zn, Cd)S phosphors for given activator concentration (1000 ppm) and CdS content from 0 to 40 per cent are illustrated in figure 5, a–e. The diffraction patterns show sharp lines indicating a high degree of crystallinity. It is important because crystalline phosphors exhibit an efficient emission when they have a high degree of crystallinity (Leverenz 1968; Chandra and Majumdar 1983). Indexing of the diffractograms was done as described earlier from which it has been found that phosphor films are of hexagonal (wurtzite) structure as CdS content is increased. The occurrence of the single phase shows that ZnS and CdS are completely soluble in each other (Burton and Hance 1976; Vankar *et al* 1978).

Figure 6 shows the variation of the lattice constants with CdS content. It is found that lattice constants a and c increase monotonically with increasing CdS content.

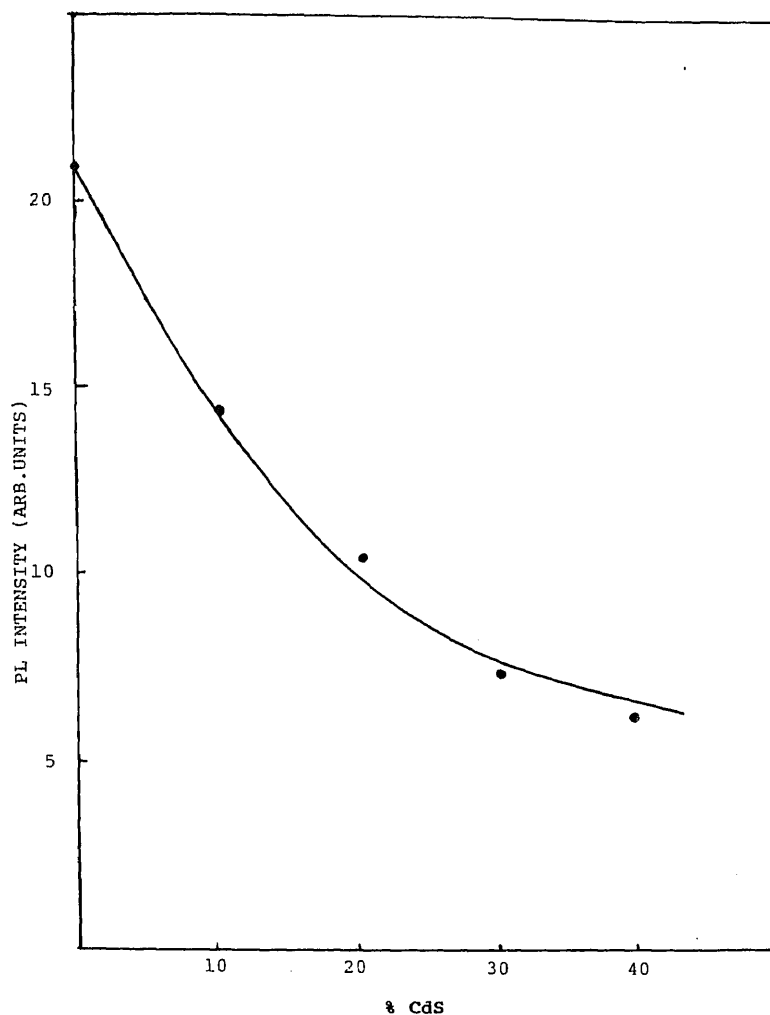


Figure 3. Effect of CdS concentration on PL intensity of (Zn,Cd)S: Au, Cl phosphors with 1000 ppm Au.

4. Discussion

In view of its importance for practical applications, a great deal of effort has been spent in the investigation of the well-known (Cu, Ag, Au) activated luminescence in ZnS phosphors (Shionoya *et al* 1964, 1965a, b; Kingsley *et al* 1965; Tripathi *et al* 1980, 1981). When a part of zinc in ZnS is replaced by cadmium, the fundamental absorption edge and the emission maximum of fluorescence band shift to the long-wavelength side, the separation between the activator level and full band remaining unchanged. The incorporation of Cd has two effects: in the right place, the Zn and Cd ions interact thoroughly, forming the fixed conduction band; in the second place, the lattice constant is increased, resulting in a decrease of the electrostatic

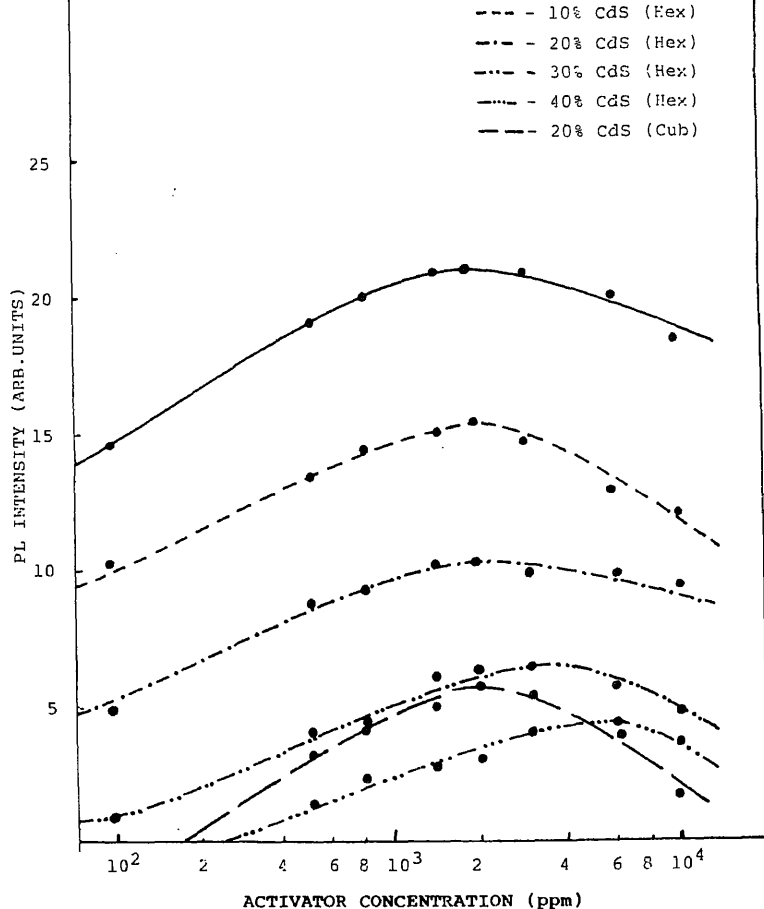


Figure 4. Effect of activator concentration on PL intensity of (Zn, Cd)S: Au, Cl phosphors.

forces and therefore in lowering of the levels of electrons at positive ions and a rise of the levels of electrons at negative ions (Leverenz 1968; Chandra *et al* 1981).

When the amounts of activator gold and co-activator chloride are of the same order, the long-wavelength band dominates. If, on the other hand, the activator concentration is much higher than that of the co-activator, then the short-wavelength band dominates. It has been shown in ZnS containing Au with Cl that although the incorporation of the activator ions is governed by the principle of charge compensation resulting in the formation of solid solution of ZnS-AuCl, the metal ion and halogen need not necessarily occupy neighbouring sites in the lattice. Therefore, there are still three possibilities for the fluorescence, viz. (i) the activator A^+ with its neighbours, (ii) the halogen X^- with its neighbours, and (iii) A^+X^- with neighbours.

The second possibility is ruled out by the fact that ZnS activated with Au or Zn shows different bands, while on the other hand the peaks of systems containing different halogens do not show the slightest difference (Chandra *et al* 1981). The third

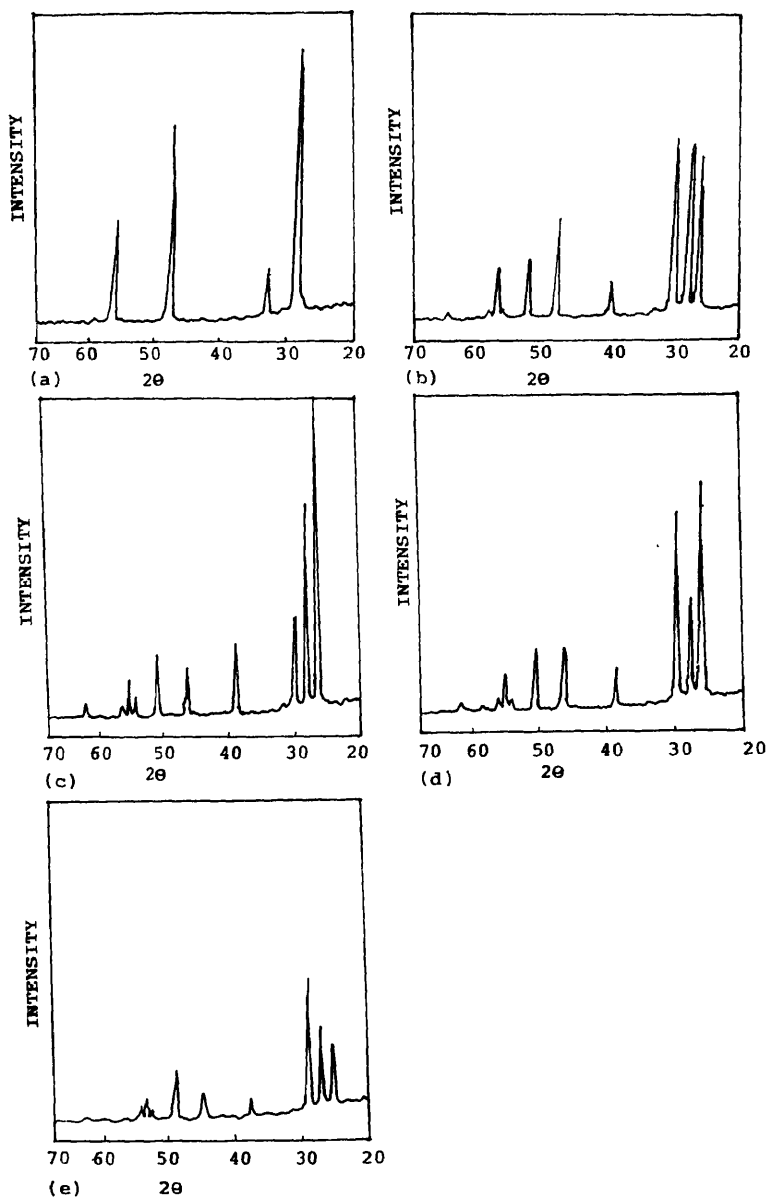


Figure 5. X-ray diffraction patterns for (Zn,Cd)S: Au, Cl phosphors with 1000 ppm Au and CdS concentration of (a) 0%, (b) 10%, (c) 20%, (d) 30% and (e) 40%.

possibility can also be discarded: if ions as different as Cl^- were to belong to the centre, marked differences should be expected. Therefore, only the first possibility remains open, and it must be concluded that this represents the actual situation where the centres of fluorescence consist of monovalent activator ions surrounded by four surplus ions. The fluorescence caused by Au and Zn is known to be due to an electronic transition between the conduction band or a defect level close to this band (Leverenz 1968).

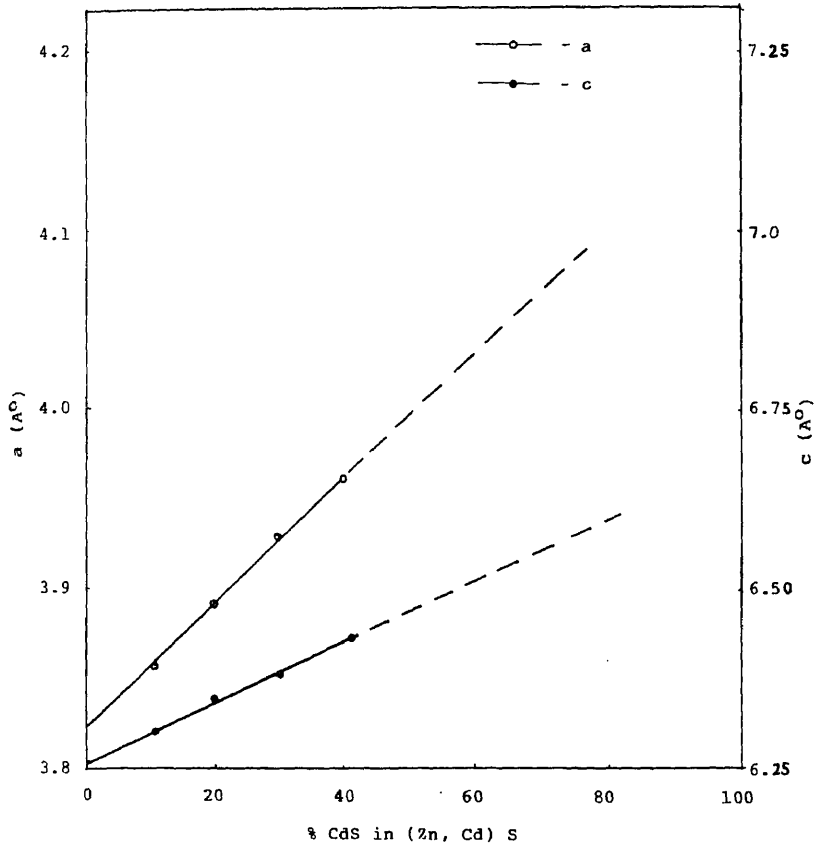


Figure 6. Variation of lattice constants a and c with CdS content in hexagonal (Zn, Cd)S: Au, Cl phosphors.

X-ray diffraction data show that the 100% ZnS baked at 1050°C for half an hour is a mixture of blende and wurtzite forms, the blende proportion being the greater. The mixed crystals ZnS + CdS are also mixtures of blende and wurtzite; the wurtzite proportion was found to be greater and increased linearly as the amount of CdS increased.

In addition, the X-ray diffraction study shows that the lattice constants a and c increase regularly with increasing CdS content. On the other hand, the ratio c/a decreases with increasing CdS content. The ionic radii of zinc and cadmium atoms are 0.074 nm and 0.097 nm respectively (Abdel Kader and Elknoly 1990). The increase in the values of the lattice parameters a and c with increasing CdS concentration in the hexagonal gold-doped (Zn, Cd)S phosphors is attributed to the larger size of the cadmium ion compared to that of zinc ion.

It has been found that the PL intensity is maximum for a particular concentration of activator in the phosphor. When the activator concentration is increased, initially the number of luminescence centres increases, hence the PL intensity increases. Later, when the activator concentration increases beyond a certain level, concentration

Photoluminescence of (Zn, Cd)S mixed phosphors
 The photoluminescence of (Zn, Cd)S mixed phosphors. The emission starts and the efficiency of radiation transition decreases. In the gold-doped (Zn, Cd)S mixed phosphors, the lattice parameters increase linearly with Cd ion content resulting in decrease of the band gap. As a matter of fact, the peak of PL spectra shifts towards longer-wavelength side with increasing CdS content in (Zn, Cd)S phosphors.

Conclusion

The shift in emission band energy due to increasing CdS concentration is very important for industrial applications such as in cathode ray tubes for television and electroluminescent devices. The desired emission band (colour) can be obtained by adjusting the ZnS/CdS ratio in (Zn, Cd)S: Au, Cl phosphors. The (Zn, Cd)S: Au, Cl phosphors containing appreciable amounts (20%) of CdS are crystallized in the hexagonal structure. In contrast, the lattice constants a and c for hexagonal structures are found to increase with increasing CdS concentration.

Acknowledgements

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Spectrophotometric determination of Ce(IV) using *o*-phenylenediamine in steels

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Abstract. A simple and sensitive spectrophotometric method for the determination of cerium(IV) was developed. With *o*-phenylenediamine cerium(IV) gives an orange-red colour with an absorption maximum at 470 nm. The system obeys Beer's law in the range 2 ppm to 500 ppm with a molar absorptivity of $2.4 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ and Sandell sensitivity of 0.5 ppm. Interference by various ions was studied. This method was used for the determination of cerium in low-alloy steels and the results are in good agreement with the certified values.

Keywords. Cerium; *O*-phenylenediamine; Ce(IV) in steel; spectrophotometry

1. Introduction

In a review of the literature on rare-earth additions to steel, Anderson and Spreadborough (1967) concluded that rare earths improve the quality and some mechanical properties of various types of steels, but that the exact effect depends on the nature of the steel. In general rare-earth additions to low-alloy steels improve the mechanical and plastic properties, besides acting as strong desulfurizing and deoxidizing agents (Kippenhan and Gschneidner 1970); whereas oxidation resistance and scaling resistance increase in the case of high-alloy steels. Addition of cerium alone increases the life of the steel. The amount of cerium added is critical and an excess is reported to have an adverse effect on high-temperature properties of steel (Trusou *et al* 1963).

The unique similarity in the chemical properties of the rare-earth group of elements has led to reliance on measurements of physical properties in order to obtain analytical data on mixtures of these elements. Various spectroscopic techniques have proven to be very useful (Fassel 1960) and among these optical emission spectroscopy has been the most widely used. However, the arc and spark emission spectra of the rare-earth elements are very complex and often consist of thousands of lines. As a result, line interferences are frequent and, even when high-dispersion instruments are used, interference-free lines are often difficult to find. Investigators were therefore led to explore the analytical capabilities of conventional flame which produces less complex spectra (Dean and Rains 1975).

Despite various attempts, it was not possible to determine cerium by atomic absorption spectroscopy (AAS) for a long period (Welz 1985). Kinnunen and Lindsjoe (1967) emphasized the difficulties in locating the proper rare-earth absorption line because of the complexity of the spectra emitted by hollow cathode lamps. They also reported that absorbance of several of the rare-earth elements was depressed significantly in the presence of fluoride and silicon. An indirect method (amplification

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reaction) has been reported for cerium by measuring molybdenum in molybdocero-phosphoric acid by AAS (Johnson *et al* 1973).

Traces of cerium are determined by titrimetric, kinetic, spectrophotometric (Sarma 1956; Papa *et al* 1959; Zhivopistsev and Parkacheva 1963; Pollock 1969; Arora *et al* 1980) and fluorimetric methods (Armstrong *et al* 1963; Kirkbright *et al* 1965, 1966; Cukor and Weberling 1968; Pal *et al* 1977; Poluektov *et al* 1970). Spectrophotometric determination in the visible range is best suited in routine analysis as the results are reproducible and the colour change can be conspicuously seen. A number of reagents are available for the spectrophotometric determination of cerium, such as brucine (Shemyakin and Volkova 1939), thenoyltrifluoroacetone (Hiroshi and Yukio 1965) and salicylhydroxime (Poddar *et al* 1965).

o-Phenylenediamine gives an orange colour with cerium(IV). The reaction is very sensitive and the colour is stable for quite a long time. Ce(III) does not give this test and hence does not interfere. A study of the above reaction was made for the spectrophotometric determination of Ce(IV) and the results are presented in this paper.

2. Experimental

2.1 Apparatus

Absorbance measurements were made with a Shimadzu 2100 S double beam UV-Vis spectrophotometer. pH measurements were made on a Unitech UI-11p pH meter.

2.2 Reagents

All reagents were of analytical reagent grade unless specified otherwise.

Cerium(IV) stock solution: 0.288 g of cerium(IV) sulphate was dissolved in 5 ml of sulphuric acid and made up to 100 ml to make a stock solution of 1000 ppm of Ce(IV). The solution was standardized gravimetrically (Vogel 1961).

o-Phenylenediamine (OPD) solution: 0.1% solution of the reagent was prepared by dissolving 100 mg of OPD (Koch-Light Laboratories Ltd, England) in 100 ml of distilled water and stored in an amber glass bottle.

2.3 Procedure

To 5 ml of 0.1% reagent (OPD) 2 ml of 1 M H_2SO_4 was added and the mixture was shaken well for 2 min. One ml of Ce(IV) solution containing 7 ppm to 500 ppm was added to the above solution. The mixture was made up to 10 ml with water and kept for 10 min to ensure complete reaction. The absorbance of the orange-red solution was measured against a similarly prepared reagent blank at 470 nm.

3. Results and discussion

The orange-red colour develops immediately on addition of reagent and the product is stable for 24 h.

Ce(IV)-OPD mixture showed maximum absorbance in the range 1 M to 3 M of H_2SO_4 after which the absorbance decreased. Five ml of 0.1% reagent was found to give maximum absorbance above which there was no significant increase in the absorbance.

The absorption spectrum of orange-red Ce(IV) and OPD products shows maximum absorbance at 470 nm, with a molar absorptivity of $2.4 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$. The system obeys Beer's law in the range 7 ppm to 500 ppm. Sandell sensitivity (Sandell 1959) of the colour was found to be 0.5 ppm of Ce(IV) at 470 nm.

Effect of diverse ions

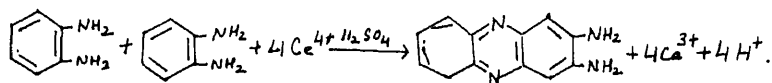
Effect of various ions on the determination of Ce(IV) by this method was examined. Fifty-fold excess of citrate, oxalate and tartrate showed no interference. Acetate, carbonate, fluoride, phosphate, bromate, iodate, chloride, sulphate, nitrate, acetate and thiourea did not interfere. Hundred-fold excess of Pb, Cd, Mn, Al, Ti, Mo, W and U; fifty-fold excess of Co, Ni and Zn; and twenty-fold excess of Bi, Sn, Zr and Th did not interfere. Fe(II), Fe(III), Cr(III) and EDTA interfered seriously. Ce(III), La(III), Gd(III), Tb(III), Ho(III), Yb(III) and Dy(III) did not interfere.

Precision

The precision of the determination of Ce(IV) by the present method was evaluated by analysing replicate samples containing different concentrations of Ce(IV) (each determination was carried out six times). The relative standard deviation in the range 10–100 ppm of Ce(IV) indicates that the method is very precise.

Composition and mechanism

Smith's (1928) method of continuous variation shows no complex formation which is confirmed by IR spectra. Hence the most possible mechanism can be the oxidation of OPD by Ce(IV). The oxidation product formed can be a diaminephenazene. The possible reaction is:



Analytical application

Solution of steels: Weigh (0.25 g) of the steel sample and transfer it to 250 ml beaker. Add 30 ml of HCl (sp. gr. 1.13) and heat till sample is dissolved. Add HNO_3 dropwise continuously, avoiding any excess, until iron is just oxidized, indicated by light effervescence. Boil the solution till the fumes are clear. Cool the solution. Iron and manganese were separated (Luke 1966; Burkin 1980) prior to the determination of Ce(IV). The solution (free from iron and manganese) was boiled with H_2SO_4 and $(\text{H}_4)_2\text{S}_2\text{O}_8$ so as to ensure complete oxidation of Ce(III) to Ce(IV). Ce(IV) in the

Table 1. Analysis of low-alloy steels for cerium.

Steel sample/composition (%)	Certified value (%)	Cerium found* (%)	
		Present method	AAS [#]
(A) ST02-1 C = 0.101; Si = 0.64; Mn = 0.22; S = 0.0048; Cu = 0.070; Ni = 0.082; Cr = 4.10; Mo = 0.53; V = 0.41; Ti = 0.029; Co = 0.018; Sn = 0.066; Nb = 0.11; Sb = 0.010; Ta = 0.063	0.0580	0.0562	0.0578
(B) ST03-1 C = 0.159; Si = 0.46; Mn = 0.75; S = 0.010; Cu = 0.67; Ni = 0.17; Cr = 3.23; Mo = 0.39; V = 0.019; Ti = 0.062; Co = 0.15; Sn = 0.046; Nb = 0.069; Sb = 0.011; Ta = 0.012	0.0120	0.0117	0.0118
(C) A-1 C = 1.01; Al = 0.01; Ni = 4.00; Ti = 0.27; Nb = 0.200; Pb = 0.036; W = 0.16	0.0240	0.0240	0.0243

*Average of six determinations

[#]Johnson *et al* 1973

solution was determined by the proposed method. The results show fairly good agreement between the proposed method and the certified value (table 1).

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Correlation analysis of isothermal crystallization of long paraffins

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Abstract. The small-angle X-ray scattering (SAXS) curves for ultralong *n*-alkanes obtained by Ungar and Keller at different times after reaching the crystallization temperature have been Fourier analysed. The correlation curves so obtained at different temperatures and different annealing times reflect sensitively all those morphological features which are broadly characteristic of the scattering curves. In addition the correlation curves clearly show a transition from a non-integer-fraction length to extended chain structure. Crystalline and amorphous lengths, degree of order and half-widths which characterize kinetics of morphological changes are also reported.

Keywords. Correlation function; long paraffins; morphological features; degree of order; non-integer fraction.

Introduction

Long *n*-alkanes, with strictly uniform chain lengths, are ideal polymeric systems. Morphological studies on such systems have revealed important details of the crystallization behaviour of polyethylene (Keller *et al* 1991). In an *in situ* X-ray diffraction study by Ungar and Keller (1986), it was observed that the initial products of crystallization were relatively imperfect crystals, with a large disordered layer, the thickness (*l*) being a non-integer fraction (NIF) of the fully extended chain (*E*) length. Further, on isothermal crystallization, the crystal perfected itself with fold length increasing to integer fraction (IF) of the chain length *L* with the degree of surface order decreasing. Position correlations provide a very neat approach to morphological studies (Glatter and Kratky 1982; Vonk and Pijpers 1985; Wlochowicz 1992) because Fourier transform of SAXS augments the characteristic features. In the present work correlation function is used to investigate the morphological changes during NIF–IF transformation in *n*-alkane C₂₄₆H₄₉₄. The characteristic features of a series of correlation curves at different times at a certain crystallization temperature are interpreted. The degree of crystal perfection and disordered layer thickness are followed by calculating crystalline and amorphous lengths and crystallinity by volume. The presence of a characteristic length marks the transition from NIF to IF state. The variation of the SAXS invariant *Q* with time and half-width of the first subsidiary maximum of correlation curves enables a clearer understanding of macromolecular crystallization.

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2. Theory

2.1 The experimental correlation function

The intensity function $i(s)$ in reciprocal space, representing the intensity of small-angle scattering from a single region of parallel layers along normal direction, is given by

$$i(s) = 2V \int_0^\infty \gamma'(x) \cos(2\pi xs) dx, \quad (1)$$

where

$$\gamma'(x) = \int_0^\infty \eta(\xi - x) \eta(\xi) d\xi, \quad (2)$$

and $s = 2 \sin \theta / \lambda$, V the irradiated volume of the region under consideration, x the coordinate perpendicular to the layer, θ the half-angle of diffraction, λ the wavelength of X-rays, and $\eta(\xi)$ the local fluctuations of electron density around the average value.

Fourier transformation of (1) gives

$$\gamma'(x) = (1/2V) \int_0^\infty i(s) \cos(2\pi xs) ds, \quad (3)$$

and

$$\gamma'(0) = \langle \eta^2 \rangle = (1/2V) \int_0^\infty i(s) ds, \quad (4)$$

is the average of the square of the electron density fluctuations. Following Debye and Bueche (1949) we define one-dimensional correlation function as

$$\gamma(x) = \frac{\langle \eta_1 \eta_2 \rangle}{\langle \eta^2 \rangle} = \frac{\gamma'(x)}{\gamma'(0)}. \quad (5)$$

The values of $\gamma(x)$ range from -1 to $+1$.

When all orientations of the layers are present the measured intensity $I(s)$ shows spherical symmetry and the following relation can be written:

$$I(s) \sim i(s)/4\pi s^2. \quad (6)$$

From (3) to (6) the position correlation function $\gamma(x)$ is given by

$$\gamma(x) = \frac{\int_0^\infty s^2 I(s) \cos(2\pi xs) ds}{\int_0^\infty s^2 I(s) ds}. \quad (7)$$

2.2 The correlation function calculated from a model

A model of alternate high- and low-electron-density regions, designated as crystalline and amorphous layers respectively, proposed by Vonk and Kortleve (1967) and

imply that the layer is entirely crystalline or amorphous. The probability distributions of crystalline and amorphous regions (x_c and x_a) are assumed to be Gaussian with mean values C and A . The corresponding probability distribution functions are given by

$$P_c(x_c) = \frac{1}{\sqrt{2\pi}} \frac{1}{\Delta C} \exp\left[-(1/2)\left[(x_c - C)/\Delta C\right]^2\right], \quad (1)$$

$$P_a(x_a) = \frac{1}{\sqrt{2\pi}} \frac{1}{\Delta A} \exp\left[-(1/2)\left[(x_a - A)/\Delta A\right]^2\right], \quad (2)$$

ΔC and ΔA are widths of these functions.

Crystallinity by volume, ϕ , is defined as

$$\phi = \frac{C}{C + A}.$$

The position correlation function for a two-phase model, following the treatment of *Debye et al* (1957), is given by

$$\gamma(x) = \frac{p_{cc}(x) - \phi}{1 - \phi},$$

where $\gamma(x)$ indicates the probability that if one end of a hypothetical measuring rod of length x is in the crystalline region then the other end is also in one of the crystalline regions.

$$p_{cc}(x) = q_c(x) + q_{cac}(x) + q_{caac}(x) + \dots, \quad (3)$$

where $q_c(x)$ indicates the probability with its subscript denoting the type of regions intersected by the measuring rod.

The probability, $q_c(x)$, of both the ends of the measuring rod being in the same region, is given by (figure 1a)

$$q_c(x) = (1/C) \int_x^\infty (x_c - x) P_c(x_c) dx_c. \quad (4)$$

In order to make contribution to $q_{cac}(x)$ the measuring rod must be positioned as in figure 1b.

The corresponding normalized distribution function is

$$P_{cac}(x) = \overbrace{Q(x_1)}^{(1)} \overbrace{P_a(x_a)}^{(2)} \overbrace{Q(x_2)}^{(3)}, \quad (5)$$

where the sign () indicates the convolution process and $Q(x_1) = Q(x_2)$. Since a length x_1 can occur only in those layers for which $x_1 \leq x_2$, $Q(x_1) = 0$ after differentiation is given by

$$Q(x_1) = (1/C) \int_{x_1}^\infty P_c(x_c) dx_c. \quad (6)$$

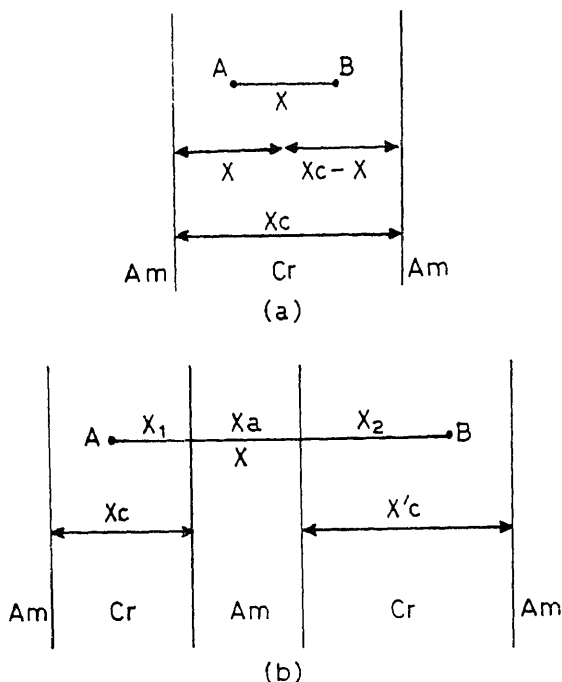


Figure 1. Positions of the measuring rod AB, which contributes to (a) q_c and (b) q_{cac} .

It can be shown that

$$q_{cac}(x) = CP_{cac}(x). \quad (16)$$

Similarly

$$q_{cacac} = CP_{cacac}(x), \quad (17)$$

where

$$P_{cacac}(x) = \widehat{Q_c} \widehat{P_a} \widehat{P_c} \widehat{P_a} \widehat{Q_c},$$

Therefore (11) can be written as

$$\gamma(x) = [1/(1 - \phi)] \{q_c(x) + CP_{cac}(x) + CP_{cacac}(x) + \dots - \phi\}. \quad (18)$$

In the present work the situation is much simplified by the use of a theorem according to which if two variates are distributed normally their sum is also distributed normally (Pipes and Harvill 1970). This theorem has the scope of being extended to the variation of the sum of three or more variates.

Thus

$$\begin{aligned} \widehat{P_a} \widehat{P_c} \widehat{P_a} = P_{a+c+a} &= \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{[\Delta C^2 + 2 \times \Delta A^2]}} \\ &\times \exp \left[- (1/2) \left(\frac{x - C - 2A}{\sqrt{[\Delta C^2 + 2 \times \Delta A^2]}} \right)^2 \right], \end{aligned} \quad (19)$$

ch gives the normalized probability distribution function for the distribution of sum of the thicknesses of two amorphous and a crystalline layer ($x_a + x_c + x_a = x$) and the mean value $A + C + A = C + 2A$.

Similarly distribution functions P_{acaca} etc can be written.

Equation (18) can now be rewritten as

$$\gamma(x) = [1/(1 - \phi)][q_c(x) + CP_{ca}(x) - \phi], \quad (20)$$

where

$$P_{ca}(x) = Q_c[P_a + P_{a+c+a} + P_{a+c+a+c+a} + \dots]Q_c. \quad (21)$$

Eq. (20) is numerically solved to obtain the value of $\gamma(x)$. For this a computer program was written by us and can be provided on request. The number of terms in the square brackets of (21) depends upon the maximum length up to which the one-dimensional correlation function is to be calculated for a particular sample.

Results and discussion

Experimental curves which have been analysed are taken from the work of Ungar and Keller (1986). These curves are recorded at different times after reaching a fixed crystallization temperature. In Ungar and Keller's experimental set-up, the long dimension of the beam was parallel to the sample capillary. The primary beam intensity was monitored and corrected for variation throughout. No slit desmearing was found necessary. The quantitative data from Ungar and Keller's curves are generated by Fourier-transforming them. Corresponding correlation curves are shown in figures 2–4. The various parameters are presented in tables 1–3 (the data correspond to the curves obtained after smoothening the computer-plotted curves).

General examination of the correlation curves at a higher temperature of 120.5°C (figure 2) and data in column 2 of table 1 reveal that in the first 2.5 min the long spacing (D) increases from 208 Å to 228 Å and the peak height of first subsidiary minimum diminishes showing a transient state of thickening in which the sample behaves as an aggregate of crystallites of varying thicknesses resulting in a low value of correlation function. At 3 min the presence of two clear-cut components of different thicknesses can be made out from a shoulder at 208 Å and a new peak (peak 2) at 228 Å. From here onwards the shoulder gradually becomes less pronounced and finally disappears showing that the transformation of NIF state is complete. Simultaneously the height and sharpness of the second peak reaching a maximum shows the near completion of the newly emerged E state. All through the first minimum, the correlation curve broadens and its depth decreases showing ordering effect.

A perusal of the data given in table 1, column 5 shows a steady increase in the crystalline length (C) and a decrease in the value of A/D from 0.43 in the beginning to 0.27 at 7 min. Thus the amorphous layer thickness fraction (A/D) is maximum for the initial NIF state and its value is much reduced in the final IF state. The same can be inferred from the change in the value of degree of order (crystallinity) or volume ϕ ; column 3, table 1) from 0.57 to a final value of 0.735.

As soon as a sample reaches the melting temperature, the crystallization is initiated by the formation of nuclei and sharply defined fold lengths. The scattering curve at this stage is also narrow and broadens with time but as soon as the structure reaches the extended chain structure it is again narrow (Ungar and Keller 1986). The

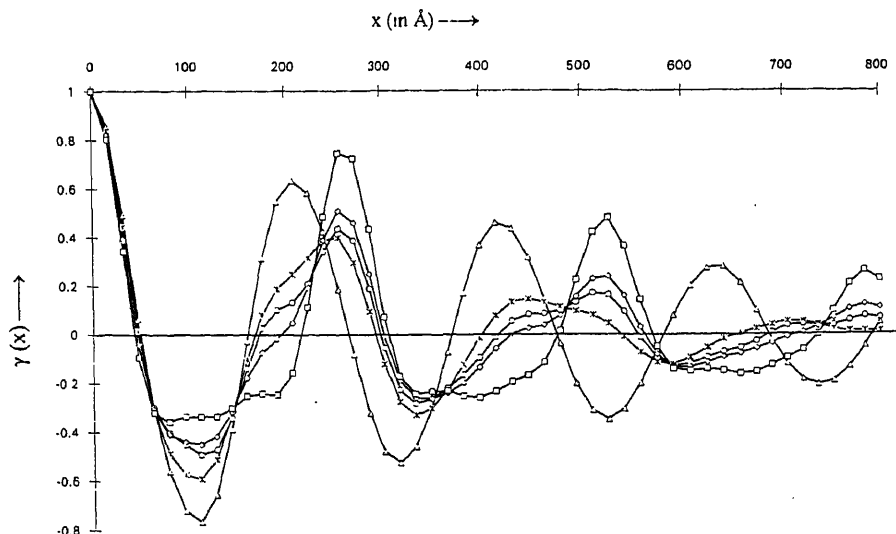


Figure 2. Experimental correlation curves of $C_{246}H_{494}$ at various times after reaching the crystallization temperature 120.5°C : 1.0 min (Δ), 3.0 min ($*$), 3.5 min ($\circ$), 4.0 min ($\diamond$) and 7.0 min ($\square$).

Table 1. Crystallization temperature 120.5°C .

Time (min)	Position of first subs. max. ($\text{\AA}$)		Degree of order (Crystallinity by volume)	Inverse of full width at half height of first subs. max. ($\times 10^{-2} \text{\AA}^{-1}$)	Parameters characteristic of two-phase parallel layer model					
	Peak 1	Peak 2			D ($\text{\AA}$)	C ($\text{\AA}$)	A ($\text{\AA}$)	A/D	$\Delta C/C$ ($\times 100$)	$\Delta A/A$ ($\times 100$)
1.0	208	—	0.570	1.39	208	118.6	89.4	0.43	15.1	14.3
1.5	208	—	0.570	1.39	208	118.6	89.4	0.43	17.4	16.3
2.0	208	—	0.587	1.28	208	122.1	85.9	0.41	21.5	18.6
2.5	228	—	0.610	1.14	228	139.1	88.9	0.39	29.5	18.9
3.0	208	252	0.630	1.25	252	158.8	93.2	0.37	28.8	20.2
3.5	208	256	0.670	1.67	256	171.5	84.5	0.33	24.4	21.6
4.0	208	260	0.690	1.73	260	179.4	80.6	0.31	22.0	20.1
7.0	—	264	0.735	2.08	264	194.0	70.0	0.27	9.2	15.2

correlation curves reflect this more sensitively, though in an inverse manner, due to the nature of Fourier transform. The inverse width of the first subsidiary maximum at half height (table 1, column 4) first decreases and then increases, thus lending support to the above fact.

The common meeting point of the various correlation curves drawn for various transient states of crystallization (at different times) shows the presence of a characteristic length which marks transition from the NIF to E state. This length is midway between the NIF and E lengths. This is better shown in figure 5 (D value vs time plot). The presence of meeting points in the negative and positive half of the correlation curve reflects only the damped oscillatory behaviour of the correlation curves.

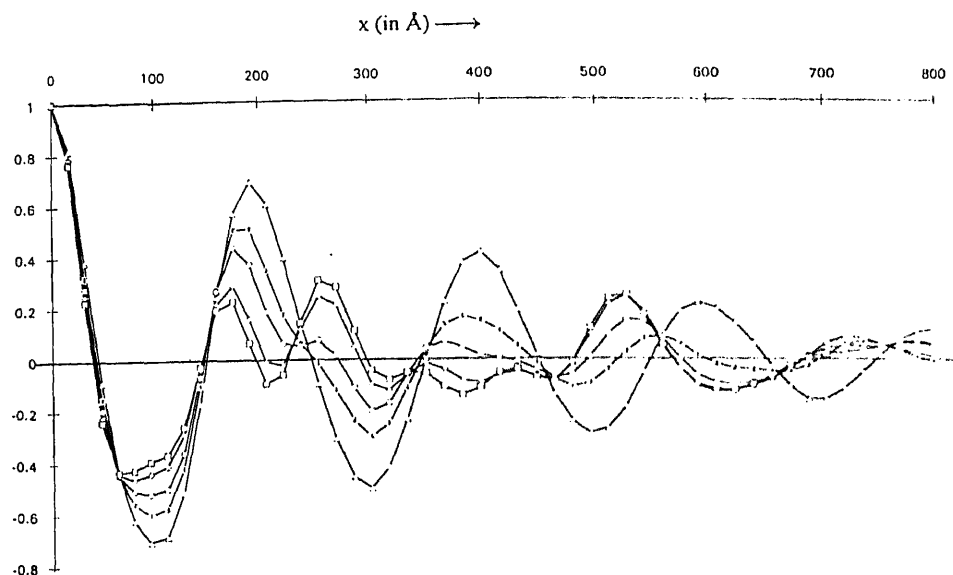


Figure 3. Experimental correlation curves of $C_{246}H_{494}$ at various times after reaching the crystallization temperature 117.8°C : 1.5 min (Δ), 3.0 min ($*$), 4.0 min ($\circ$), 6.0 min ($\odot$) and 8.0 min ($\square$).

Table 2. Crystallization temperature 117.8°C .

Position of first subs. max. ($\text{\AA}$)		Degree of order (crystallinity by volume)	Inverse of full width at half height of first subs. max. ($\times 10^{-2} \text{\AA}^{-1}$)	Parameters characteristic of two-phase parallel layer model			
Peak 1	Peak 2			D ($\text{\AA}$)	C ($\text{\AA}$)	A ($\text{\AA}$)	A/D
192	—	0.587	1.56	192	112.7	79.3	0.41
192	—	0.593	1.61	192	113.9	78.1	0.41
188	—	0.610	1.73	188	114.7	73.3	0.39
184	—	0.625	2.00	184	115.0	69.0	0.38
182	240	0.631	2.00	240	151.4	88.6	0.37
176	256	0.658	2.08	256	168.4	87.6	0.34
176	256	0.673	2.50	256	172.3	83.7	0.33
176	260	0.683	2.50	260	177.6	82.4	0.32
172	264	0.697	2.50	264	184.0	80.0	0.30

correlation curves at 117.8°C (figure 3), a somewhat lower temperature, and responding data in table 2 show the transformation occurring slowly. The two subsidiary maximum peaks can be seen clearly even after 8 min. The E structure is emerging steadily and perfecting itself slowly. The spacing of the still untransformed is slowly decreasing and tending to the spacing corresponding to the once folded structure. The fact that the height of peak 1 decreases continuously shows that the

choice of acquiring an extended chain structure seems to be the most preferred one leading to a final E structure. It is further confirmed by the presence of a prominent second subsidiary maximum at 520 Å. The positive values of the correlation function at the two meeting points of the curves at 152 Å and 240 Å (average value) indicate the tendency of the system to either fold in two (F2 structure) or have extended chain disposition (E structure).

At a still lower temperature of 106°C the correlation curves (figure 4, also table 3) indicate the further slowing down of the NIF-IF transformation. The common meeting point of curves at about 164 Å shows that a decrease of the repeat distance will follow, leading to a once folded structure in this case.

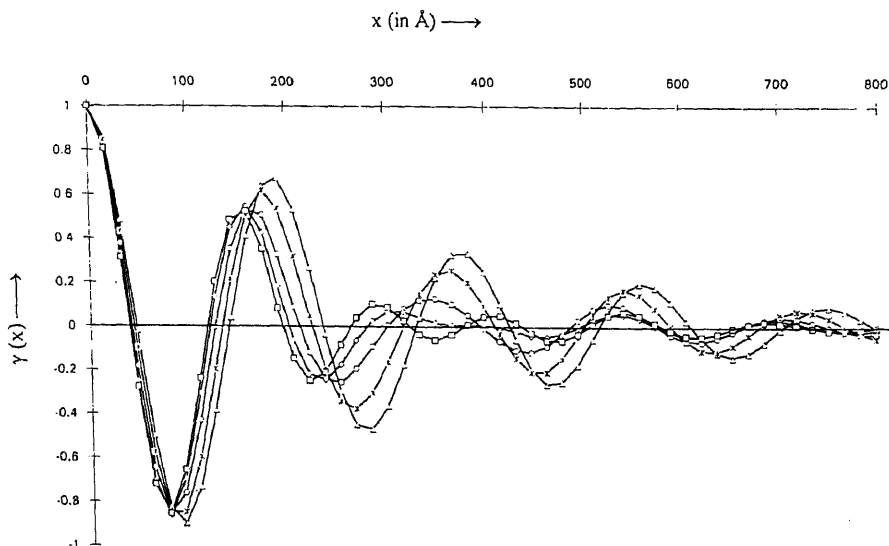


Figure 4. Experimental correlation curves of $C_{246}H_{494}$ at various times after reaching the crystallization temperature 106°C: 0.2 min (Δ), 2.5 min (*), 8.5 min ($\circ$), 18.0 min ($\diamond$) and 33.0 min ($\square$).

Table 3. Crystallization temperature 106.0°C.

Time (min)	Position of first subs. max. (Å)		Degree of order (crystallinity by volume)	Inverse of full width at half height of first subs. max. ($\times 10^{-2} \text{Å}^{-1}$)	Parameters characteristic of two-phase parallel layer model			
	Peak 1	Peak 2			D (Å)	C (Å)	A (Å)	A/D
0.2	188	—	0.526	1.56	188	98.9	89.1	0.474
2.5	176	—	0.538	1.67	176	94.7	81.3	0.462
8.5	164	—	0.540	1.73	164	88.6	75.4	0.460
18.0	160	—	0.537	2.00	160	85.9	74.1	0.463
33.0	152	—	0.540	2.08	152	82.1	69.9	0.460

Thus the correlation approach shows that the transformation of the metastable β' state to a more ordered and more stable extended state takes place by the thickening of the lamellae and the thinning of the disordered layer surface (at 120.5°C and 117.8°C) while in case of transformation to once folded state a decrease in long period takes place mainly by a decrease in the value of amorphous length. The process is known in polymers as secondary crystallization.

Figures 6 and 7 show a plot of integrated SAXS intensity vs time at fixed temperatures 120.5°C and 117.8°C. The fact that the invariant Q first increases and then decreases indicates that during isothermal crystallization the ratio between the thicknesses of amorphous and crystalline layers decreases.

In their work on $C_{246}H_{494}$, Ungar and Keller (1987) have shown that the stepping of the primary crystal growth rate of extended chain crystals is triggered by the thermal F-E transformation at about 121.2°C, the transition temperature between extended and folded chain crystallization. Therefore in the present temperature range

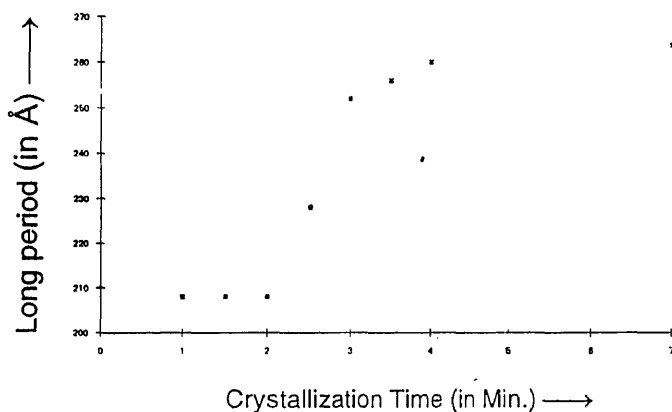


Figure 5. Long period vs crystallization time plot for isothermal crystallization of $C_{246}H_{494}$ at 120.5°C.

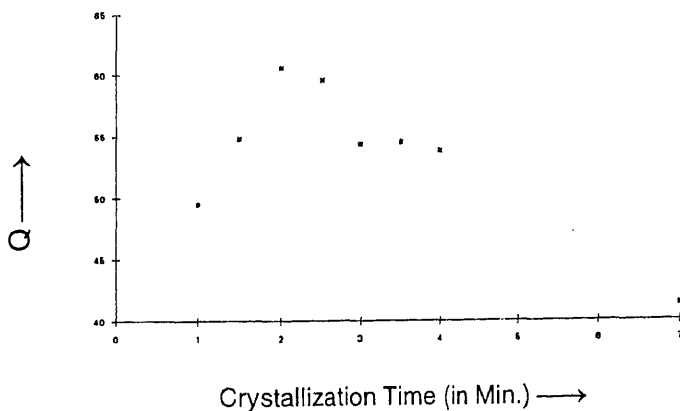


Figure 6. SAXS invariant (Q) vs crystallization time plot for isothermal crystallization of $C_{246}H_{494}$ at 120.5°C.

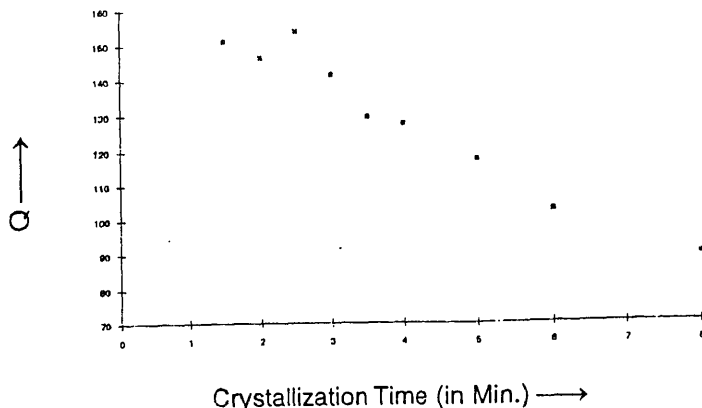


Figure 7. SAXS invariant (Q) vs crystallization time plot for isothermal crystallization of $C_{246}H_{494}$ at 117.8°C .

the E-chain form is the result of thickening of the initially formed crystals and not of direct crystallization. The perfection is thus the result of an increase in crystalline-layer fraction of the crystal with a concomitant decrease of noncrystalline-layer fraction.

The degree of order or disorder obtained from the correlation function includes the order or disorder present in the folds. As the system makes a transition to the extended state, the order increases. For a tight fold on the surface a minimum of ten repeat units at both the ends are necessary (Young 1986) and in tight folding the chains would become part of the ordered state. The disordered state would really arise from the fold lengths greater than ten (at both the ends) and these will constitute loose ends in fold length.

A possible explanation of the thickening of the lamellae in the above manner is that the sliding diffusion of the molecular chains along their axes compacts them in the crystalline layer of the crystal to the surface of which they are attached, as in the case of *trans*-1,4-polybutadiene (Tatsumi *et al* 1967). A molecular kink, a unique type of point defect for macromolecules (Young 1986), moving along the chain may be the mechanism of crystal thickening.

The presence of a disordered layer surface all through the isothermal crystallization from NIF to IF state (at temperatures examined) shows that there are at least some of the folds which, being linked with different crystalline regions, remain so even after the crystal has perfected itself.

The experimental studies have also been compared with the theoretical calculations from the parallel-layer model of Vonk and Kortleve (1967) and Kortleve and Vonk (1968). The parameters of the model, viz. the crystalline and amorphous lengths and their log normal widths, were varied to obtain best fits of theoretical curves to the corresponding experimental ones. As a representative of the match between the experimental results and theoretical model we show in figures 8–11 the correlation curves for the experimental data of $C_{246}H_{494}$ at 120.5°C at 1.0, 2.5, 3.0 and 7.0 min after reaching the temperature of crystallization and theoretical model of crystalline and amorphous lengths and their widths of distribution respectively. The following conclusions could be drawn:

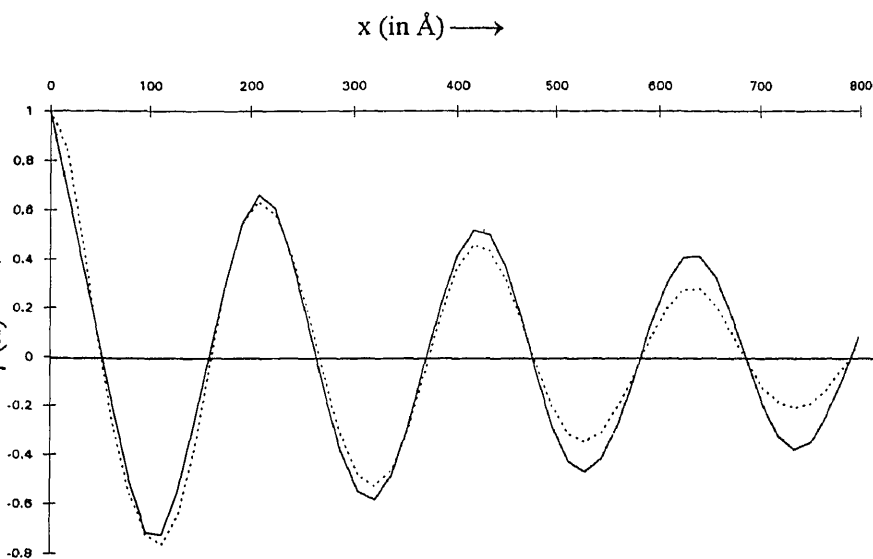


Figure 8. Experimental (---) and theoretical (—) correlation curves at 1.0 min after reaching the crystallization temperature 120.5°C.

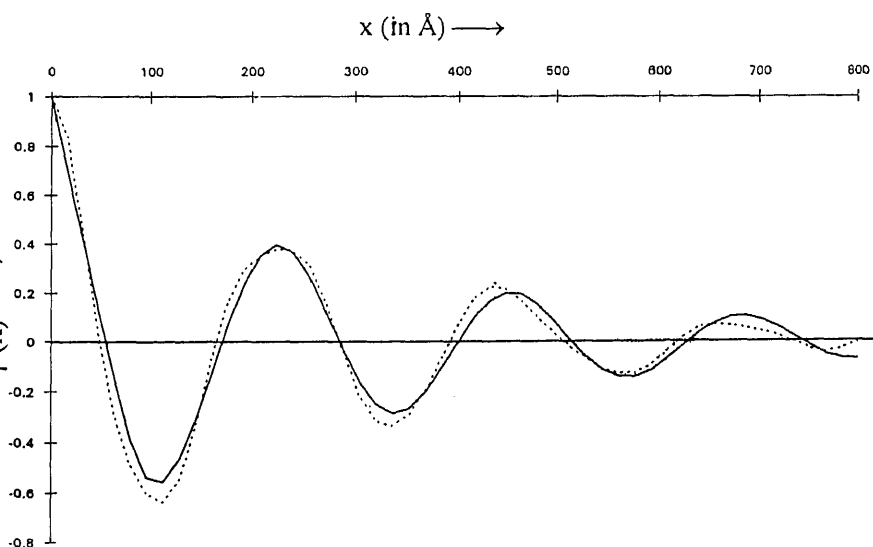


Figure 9. Experimental (---) and theoretical (—) correlation curves at 2.5 min after reaching the crystallization temperature 120.5°C.

A fairly good agreement between the theoretical and experimental curves shows suitability of the model for the calculations of the various parameters. However, there are some deviations for larger correlation lengths.

The matching between the theoretical and experimental curves gets better with thermal crystallization time (1.0 to 2.5 min) till the system is ripe for transformation. During NIF-IF transformation the system is in nonequilibrium state with distorted

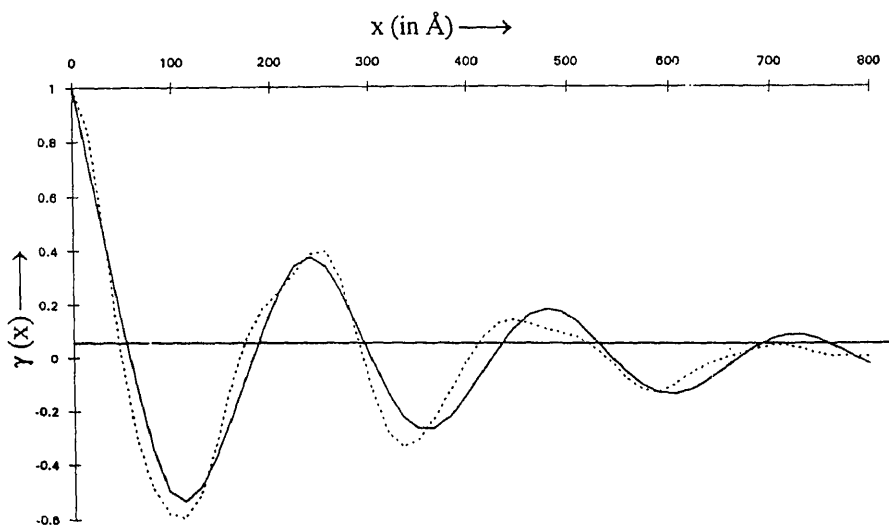


Figure 10. Experimental (---) and theoretical (—) correlation curves at 3.0 min after reaching the crystallization temperature 120.5°C.

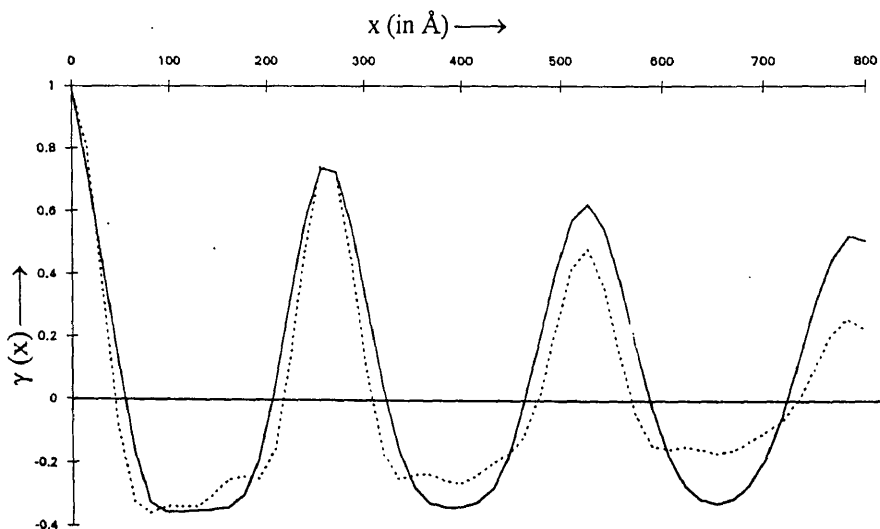


Figure 11. Experimental (---) and theoretical (—) correlation curves at 7.0 min after reaching the crystallization temperature 120.5°C.

layer surfaces and as expected does not follow the model. The matching is excellent at 7.0 min at least up to first subsidiary maximum showing the emergence of a perfected IF structure (Ungar and Keller 1986).

The variation of the width of distribution of crystalline layer, which is the wider of the two layers, given by the parameter $\Delta C/C \times 100$ (table 1, column 5), brings out clearly the fact that isothermal crystallization leads to a more stable and perfect IF structure (Ungar and Keller 1986).

(iii) The fact that the experimental correlation curves show a greater damping than

theoretical ones indicates that to assign a constant value to the width of distribution of the layer thicknesses is not wholly justified owing to the nonparallelism and nonsmoothness of the layer surfaces (Vonk 1973).

The nonzero value of $[\partial^2 \gamma(x)/\partial x^2]$ at origin indicates the probability of a transition over but due to the limited accuracy of the correlation curves in this region this could not be taken into account.

Notwithstanding the above factors the present analysis lends support to the two-phase concept of a polymer.

A detailed study on the theoretical matching of the experimental calculations will be reported in a communication to follow.

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